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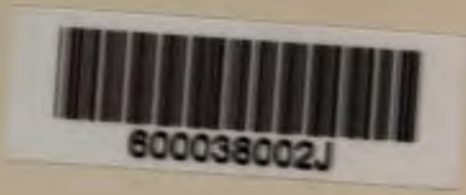
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PRINCIPLES

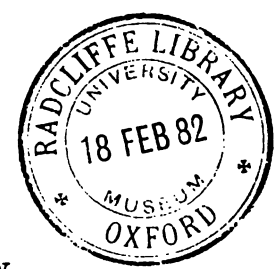
OF

CHEMICAL PHILOSOPHY.

BY

JOSIAH PARSONS COOKE,

Erving Professor of Chemistry and Mineralogy
in Harvard College.



REVISED EDITION.

London:
MACMILLAN AND CO.
1882.

TO

CHARLES WILLIAM ELIOT,

President of Harvard College,

THIS WORK IS DEDICATED,

AS A TOKEN OF

WARM REGARD AND LONG FRIENDSHIP.

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PREFACE.

CHEMISTRY may be studied from two wholly different aspects. In the first place, it is peculiarly an experimental science; and the experimental method by which its facts and principles have been developed is at once its most conspicuous and its most attractive feature. Moreover, it is this very feature which renders the study of chemistry such an important means of education. As a collection of valuable facts, chemistry has no greater claims to be included in a course of liberal culture than many other branches of knowledge, and it is at best a very unfruitful field for the exercise of the memory. But, on the other hand, there is no study which is better adapted to cultivate the powers of observation, and to train the mind in the inductive method of studying nature, than this. Hence, chemistry should always be approached from the experimental side, and its facts and principles should be directly associated with the experimental evidence on which they are based. Indeed, it is not possible to obtain an accurate and real knowledge of these elements of the science except at the laboratory table, or where the student is brought directly in contact with the facts of nature. The method of instruction should be that of object teaching from the first, and although the study may be directed by good books, like Nichols's Abridgment of Eliot and Storer's Manual, it must be remembered that no description of phenomena, however vivid, can ever produce on the mind the impression of the phenomena themselves.

In the second place, however, the science of chemistry is a philosophical system, by which the observed phenomena and

empirical principles have been classified and correlated; and, after the student has become personally acquainted with the fundamental facts, it is essential for any further advancement in the study that he should comprehend this system. Thus alone can he give breadth and dignity to his knowledge, and come to know nature, not as a sum of certain parts, but as a grand and related whole. Such a generalized knowledge of chemistry this book aims to impart. It presents chemistry as a philosophical system, and it deals with the facts of the science only so far as they illustrate this system. It is not intended in any respect to take the place of laboratory teaching, but solely to supplement it. Not until the student has become familiar with chemical phenomena, at least to some limited extent, is he prepared to study the science in a systematic way; but all who have this preparation will acquire most rapidly a general knowledge of the whole field when the subject is presented in a deductive form. The author has had especially in view this class of students, and has endeavored to meet their wants.

Part I. of the book contains a statement of the general laws and theories of chemistry, an explanation of its nomenclature and mode of symbolical notation, together with so much of the principles of molecular physics as are constantly applied in chemical investigations. It might be figuratively called a grammar of the science. It is intended to be studied independently, in consecutive lessons, and is adapted for class-room recitations, which should be accompanied, however, by such experiments or further explanations as the teacher may find necessary to render the subject intelligible.

Part II. of the book presents the scheme of the chemical elements. It should only be studied in connection with experimental lectures or laboratory work, and will be found chiefly useful for systematizing and reviewing the phenomena observed in the lecture-room or laboratory. It is a note-book which not only records the most important facts, but also connects them in

such a way that they can be most readily comprehended and remembered. Since Qualitative and Quantitative Analysis form such important subjects of laboratory teaching, it has been made a special point to illustrate those relations of the elements, often subordinate, on which analytical processes depend.

The value of problems as means of culture and tests of attainment can hardly be overestimated, and they have therefore been made a chief feature in this book. Since those here given are chiefly intended as guides to the student, the answers have usually been added; and where the method was not obvious, the chief steps in the solution have been given as well. Every teacher will be able to multiply problems after these models to suit his own requirements.

The questions which accompany the problems form another essential feature in the plan of instruction here presented. They are intended, not only to direct the student's attention to the most important points, but also to stimulate thought by suggesting inferences to which the principles stated legitimately lead. These questions, moreover, will indicate to the teacher the manner in which it is intended that the book should be studied.

In arranging the chapters of Part I., the only aim has been to present the several subjects in a logical sequence. In other respects the order adopted is not always the most philosophical; but the teacher can of course vary the order at pleasure. So, also, in regard to Part II., the teacher may prefer to take up the elements in his lectures in a different order from that in which they are there classified; but then the several "Divisions" may be studied in any order a teacher would be likely to adopt, with equal advantage.

In revising the book for this edition, it has been largely rewritten, — to such an extent that it is in many respects a new book. Several subjects have been treated in a novel way, while others, which have been chiefly developed during the last ten years, are now presented for the first time. The

doctrine of special types, which had great prominence in the science when the book was first written, has given place to the more general conception of molecular structure. The distinction between artiads and perissads is no longer made a fundamental basis of classification, and more prominence is given to serial relations and the law of periodicity. The division on Organic Chemistry has been entirely rewritten, on a plan elaborated by Professor C. Loring Jackson, to whom the author is greatly indebted for this kind assistance. Professor Jackson, however, is not responsible for the form of statement which the author has made to correspond with the rest of the work. Among other recent results of chemical investigation, the new methods of determining vapor density, the principles of thermo-chemistry, the theory of dissociation, the doctrine of specific refractive power, the specific heat of elementary atoms, the relations of molecular volumes, and the principles of chemical classification, are all described in their appropriate places. In correcting the proof of this edition, the author has had the assistance of Professor W. R. Nichols, of the Institute of Technology, who has made many valuable suggestions, which have added to the accuracy and completeness of the book, and he would here express his great obligations for this most friendly service.

CAMBRIDGE, June 17, 1881.

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FIRST PRINCIPLES

OF

CHEMICAL PHILOSOPHY.

PART I.

CHAPTER I.

INTRODUCTION.

1. **Definitions.** — The *volume* of a body is the space it fills, expressed in terms of an assumed unit of volume. The *weight* of a body, as the word is used in chemistry and generally in common life, is the amount of material which the body contains compared with that in some other body assumed as the unit of weight. The *specific gravity* of a body is the ratio of its weight to the weight of an equal volume of some substance which has been selected as the standard. Solids and liquids are always compared with water at its greatest density, which is at 4° centigrade, and hence the numbers which stand for their specific gravities express how many times heavier they are than an equal volume of water at this temperature. Gases, however, are most conveniently compared with the lightest of all known forms of matter, namely, hydrogen, and in this book the number which indicates the specific gravity of a gas expresses how many times heavier it is than an equal volume of hydrogen, compared under the same conditions of temperature and pressure.

2. **Volume and Weight.** — All experimental science rests upon accurate measurements of these fundamental elements, and it is therefore very important that there should be a general agreement among scientific men in regard to them. This has

been secured by the almost universal adoption of the French system of measures and weights in all scientific investigations. The details of this system are given in Table I., and they require no further explanation. Its great advantage over our ordinary English system is not only in its decimal subdivision, but also in the simple relation which exists between the units of measure and of weight. Since the unit of weight is the weight of the unit volume of water, and since the specific gravity of solids and liquids is always referred to water, as the standard, it is always true in this system that

$$W = V \times Sp.\ Gr. \qquad [1]$$

If the volume is given in cubic centimetres, the weight obtained is in grammes; but if the volume is given in cubic decimetres (i.e. litres), the weight is found in kilogrammes. In this formula, *Sp. Gr.* stands for the specific gravity referred to water. If the specific gravity is referred to hydrogen, as in the case of gases, the value must be reduced to the water standard before using it in the formula. The reduction is easily made, by multiplying by 0.0000896, a fraction which is simply the specific gravity of hydrogen itself referred to water. Using Sp. Gr. to represent the specific gravity of a gas referred to hydrogen, the formula becomes

$$W = V \times \text{Sp. Gr.} \times 0.0000896, \qquad [2]$$

and may then be used in all calculations connected with the weight and volume of aeriform bodies. In such calculations, in order to avoid the long decimal fractions which the use of the gramme entails, Hofmann has proposed to introduce into chemistry a new unit of weight which he calls the *crith*. This unit is the weight of one cubic decimetre or litre of hydrogen gas at the standard temperature and pressure, and is equal to 0.0896 gramme. If now we estimate the weight of all gases in *criths*, and let W represent this weight, while W represents the weight in grammes, and V the volume in *litres*, we shall also have

$$\text{W} = \text{V} \times \text{Sp. Gr.} \quad \text{and} \quad W = \text{W} \times 0.0896, \qquad [3]$$

and all problems of this kind will then be reduced to their simplest terms.

The specific gravity of gases is also frequently referred to dry air, which for many reasons is a convenient standard. The weight of one litre of air under standard conditions is 1.293187 grammes. Hence, representing specific gravity referred to air by **Sp. Gr.** we have

$$\text{Sp. Gr.} : \textbf{Sp. Gr.} = 1.2932 : 0.0896,$$

or

$$\text{Sp. Gr.} = \textbf{Sp. Gr.} \times 14.42,$$

and

$$\textbf{Sp. Gr.} = \text{Sp. Gr.} \times 0.06929.$$

3. **Chemistry and Physics.** — Among material phenomena we may distinguish two classes: first, those which are manifested without a loss of identity in the substances involved; secondly, those which are attended by a change of one or more of the materials employed into new substances. The science of chemistry deals with the last class of phenomena, that of physics with the first; and hence the terms "chemical" and "physical" phenomena. An illustration will make this distinction plain. When a bar of iron is drawn out into wire, is rolled out into thin leaves, is reduced by mechanical means to powder, is forged into various shapes, is melted and cast into moulds, is magnetized, or is made the medium of an electric current, since the metal does not in any case lose its identity, the phenomena are all physical. When, on the other hand, the iron bar rusts in the air, is burnt at the blacksmith's forge, or is dissolved in dilute sulphuric acid, the iron is converted into a new substance, iron rust, iron cinders, or green vitriol, and the phenomena are chemical. The distinction between these two departments of human knowledge is not, however, so strongly marked as the definition would seem to imply. In fact they coalesce at many points, and a knowledge of the elements of physics is an essential preliminary to the successful study of chemistry. In the following pages it will be assumed that the student is acquainted with the most elementary principles of this science, and references will be made to the sections of the author's work on Chemical

Physics. The same relation which physics bears to chemistry on the one side, chemistry bears to physiology and the natural-history sciences on the other.

QUESTIONS AND PROBLEMS.

1. Reduce by Table L. —

30 inches to fractions of a metre.	Ans. 0.7619 metre.
76 centimetres to inches.	Ans. 29.92 inches.
36 kilometres to miles.	Ans. 22.38 miles.
10 metres to feet and inches.	Ans. 32 ft. 9.7 inches.
1 cubic metre to quarts.	Ans. 880.66 quarts.
1 cubic foot to litres.	Ans. 28.31 litres.
1 pint to cubic centimetres.	Ans. 567.8 $\overline{\text{c. m.}}^3$
1 litre to cubic inches.	Ans. 61.027 cubic inches.
1 pound avoirdupois to grammes.	Ans. 453.6 grammes.
1 kilogramme to ounces avoirdupois.	Ans. 35.27 ounces.
1 ounce to grammes.	Ans. 28.35 grammes.

2. If the globe were a perfect sphere, what would be the circumference and what the diameter in kilometres?

Ans. Circumference, 40.000 kilometres.
Diameter, 12,740 "

3. The length of the metre was determined by measuring the distance between Dunkirk (in France), latitude 51° 2′ 9″, and Formentera (one of the Balearic Islands), latitude 38° 39′ 56″, both on the same meridian. This distance was found by triangulation to be equal to 730,430 toises. What is the length of a metre in terms of this old French unit of measure? What, also, was the length measured in English miles? No account is to be taken of the ellipticity of the earth.

Ans. The metre, 0.5314 toise.
The length was 854 miles.

4. The *Sp. Gr.* of iron is 7.84. What is the weight of 10 $\overline{\text{c. m.}}^3$ of the metal in grammes? What is also the weight in kilogrammes of a sphere of iron whose diameter equals one decimetre?

Ans. 78.4 grammes and 4.105 kilogrammes.

5. What is the weight in grammes of 50 $\overline{\text{c. m.}}^3$ of oil of vitriol, when the *Sp. Gr.* of the liquid is 1.8? Ans. 90 grammes.

6. The *Sp. Gr.* of alcohol being 0.8, what volume in litres would weigh 7.2 kilogrammes? Ans. 9 litres.

7. Assuming that the earth is spherical, and its mean *Sp. Gr.* 5.67, what would be its weight, using as the unit of weight a kilometre cube of water at its greatest density? Ans. 6,130,000,000,000.

8. Determine the *Sp. Gr.* of absolute alcohol from the following data: weight of empty bottle, 4.326; weight of same filled with water, 19.654; weight of same filled with alcohol, 16.741.

Ans. 0.8095.

9. Determine the *Sp. Gr.* of lead from the following data: weight of bottle filled with water, 19.654; weight of lead shot, 15.456; weight of bottle filled in part with the shot and the rest with water, 33.766. Ans. 11.5.

10. Determine the *Sp. Gr.* of iron from — weight of iron in air, 3.92; weight under water, 3.42. Ans. 7.84.

11. Determine the *Sp. Gr.* of wood from — weight of wood in air, 25.35; weight of sinker under water, 9.75; weight of wood with sinker under water, 5.10 grammes. Ans. 0.845.

12. How much volume must a hollow sphere of copper have, weighing one kilogramme, which will just float in water? What must be the volume of the copper (*Sp. Gr.* of copper, 8.8)?

Ans. 1 cubic decimetre and 113.6 $\overline{\text{c. m.}}^3$

13. How much volume must a hollow cylinder of iron have, which weighs 10 kilogrammes and sinks one half in water, and what must be the volume of the metal? Ans. 20 $\overline{\text{d. m.}}^3$ and 1.276 cubic decimetres.

14. What is the weight in grammes (under standard conditions) of 128 $\overline{\text{c. m.}}^3$ of oxygen gas (Sp. Gr. = 16)? Ans. 0.1834 gramme.

15. How many litres of carbonic anhydride gas (Sp. Gr. = 22) would weigh (under normal conditions) 4.480 kilogrammes?

Ans. 2274 litres.

16. Solve the last two problems by [3], and show in what respect the method differs from that indicated by [2].

17. What is the weight in criths (under standard conditions) of one litre of nitrogen gas (Sp. Gr. = 14), of one litre of chlorine gas (Sp. Gr. = 35.5), of one litre of marsh gas (Sp. Gr. = 8), and of one litre of ammonia gas (Sp. Gr. = 8.5)?

Ans. 14, 35.5, 8, and 8.5 criths, respectively.

18. What is the weight in grammes of one litre of each of the same gases under the same conditions?

Ans. 1.254, 3.180, 0.7166, and 0.7614 grammes respectively.

19. The weight of one litre of hydrochloric acid gas is 1.642 grammes; of carbonic oxide gas 1.2500 grammes; of cyanogen gas 2.335 grammes, and of hydrogen gas 0.0896 gramme. What is the specific gravity of each of these gases referred to air?

Ans. 1.270, 0.9668, 1.806, and 0.0693 respectively.

20. What is the volume (under standard conditions) of 12.54 grammes of nitrogen gas, when the specific gravity referred to air is 0.9703? Ans. 10 litres.

21. What is the weight of one litre of air in criths?

Ans. 14.42 criths.

22. What would be the ascensional force of one thousand litres of hydrogen, under normal conditions?

Ans. The ascensional force is the difference between the weight of the hydrogen and that of the air displaced. Hence, in the present example, the ascensional force would be 14,420 − 1,000 = 13,420 criths, or 1,201 grammes.

23. What is the value of a crith in grains, English weight?

Ans. 1.382 grains.

NOTE. — The answers to the problems in this book have been obtained with the table of four-place logarithms which accompanies it, and are only accurate to the degree of precision which this table affords.

CHAPTER II.

FUNDAMENTAL CHEMICAL RELATIONS.

4. **Compounds and Elements.** — With only about seventy known exceptions, all substances, by various chemical processes, may be decomposed, and hence are called *chemical compounds;* while the seventy substances which have as yet never been resolved into simpler parts are called *chemical elements.* There is some reason for believing that many, if not all, of these elementary substances may hereafter be decomposed, and hence they can only be considered chemical elements provisionally; but however this may be, all known materials may still be regarded as formed by the union of the particles of one or more of these seventy substances. A list of the chemical elements is given in Table II. But as names have been assigned by good authorities to several assumed elements, whose existence cannot be regarded as demonstrated, these names are queried in the table. Of these elementary substances more than three fourths possess metallic properties, and among them are all the useful metals, including the liquid metal mercury. The rest present every variety of physical character. Oxygen, hydrogen, nitrogen, chlorine, and probably fluorine, are gases under ordinary conditions, although by intense cold and great pressure they have all been condensed to liquids. Bromine is a very volatile liquid; and among the solids we have every gradation between the highly volatile iodine, or the easily fusible phosphorus, on the one hand, and carbon, which has never even been melted, on the other. We find, also, among the elements every difference as regards density. Hydrogen gas is the lightest, and the metal platinum the heaviest substance known. Several of the elementary substances occur in a free state in nature, for example, oxygen and nitrogen in the atmosphere, carbon in the coal beds,

sulphur in the neighborhood of active volcanoes, iron in meteoric stones, while arsenic, antimony, bismuth, copper, gold, silver, mercury, and platinum, with a few other rare associates, are sometimes found in a more or less pure state in metallic veins. Gold and platinum are usually found in a free condition, though as a rule slightly alloyed with their associated metals; but all the other elements are generally found in combination, and the greater number appear in nature only in this condition. From such compounds the elements may be extracted by various chemical processes, which will appear as we proceed. Among these elements the useful metals are the tools of civilization, carbon is our universal fuel, while sulphur, phosphorus, arsenic, chlorine, bromine, and iodine have found important applications in the arts, and are therefore articles of commerce; but the greater number of the elements are only to be seen in the chemist's laboratory, and are solely objects of chemical investigation. The elements are distributed in nature in very unequal proportions. At least one half of the solid crust of the globe, eight ninths of the water on its surface, and one fifth of the atmosphere which surrounds it, consist of the one element, oxygen. Moreover, the other elements are usually found in combination with oxygen, so that oxygen may be regarded as the cement by which these elementary parts of the world are held together. Next in abundance is silicon, which, after oxygen, is the chief constituent of the rocks, and makes up about one fourth of the earth's crust. Silicon is always found combined with oxygen, and more than one half of the oxygen of the globe is in combination with this element. Hence, the compound of the two, which we call silica or quartz, must make up more than one half of our solid globe, at least as far as its composition is known. After silicon in the order of abundance would follow the elements aluminum, calcium, magnesium, potassium, sodium, iron, carbon, sulphur, hydrogen, chlorine, nitrogen, which, without attempting to discriminate between them, make up together very nearly the other fourth of the earth's mass; for the remaining elements — including all the useful metals except iron — do not constitute in all more than a hundredth part of it. Of the seventy known

elements, then, thirteen alone make up at least ninety-nine hundredths of the whole known mass of the earth.

5. **Analysis and Synthesis.** — The composition of a chemical compound may be made evident in two ways: first, by breaking up the compound into its constituent parts; secondly, by reuniting these parts and reproducing the original substance. The first of these methods of proof is called *analysis;* the second, *synthesis.* The study of the processes (whether analytical or synthetical) by which the composition of a body may be discovered, and the relative amounts of its various constituents determined, forms an important branch of practical chemistry, which is known, in general, as *Chemical Analysis,* and this is subdivided into Qualitative and Quantitative Analysis, according to the object in view.

6. **Law of Definite Proportions.** — Numberless analyses have proved that *any given chemical compound always contains the same elements combined in the same proportions.* Thus, when we analyze water, sugar, and salt, we always obtain the result given below; and this result is invariable, saving small errors of observation, from whatever source these materials may be drawn. The composition is given in per cents, as is usual in such cases.

Water (Dumas).		Salt.		Sugar (Péligot).	
Hydrogen,	11.112	Sodium,	39.32	Carbon,	42.06
Oxygen,	88.888	Chlorine,	60.68	Hydrogen,	6.50
	100.000		100.00	Oxygen,	51.44
					100.00

Chemists have not yet succeeded in making sugar by combining its elements, but the synthesis both of water and salt is easily effected, and illustrates still more forcibly the law we are considering. Thus we may mix together hydrogen and oxygen gas in any proportion, but when, by passing an electric spark through the mixture, we cause the elements to combine, then the gases unite in the exact proportion indicated above, and any excess of one or the other which may be present is left over. The law of definite proportions gives to chemistry a mathemati-

cal basis; for, since the analyses of all compounds have been made and tabulated in a way that will be soon explained, it is always possible, when the weight of a compound is given, to calculate the weights of its constituents, and, when the weight of one of its elements is known, to calculate the weights of all the other elements present.

7. **Mixture and Chemical Compound.** — The law of definite proportions gives a simple criterion for distinguishing between a mixture and a true chemical compound. In the first the elements may be mixed in any proportion, but in the true compound they are always combined in definite proportions. Thus we may mix together copper filings and sulphur in any proportion, but as soon as we apply heat, and cause the elements to combine, then the copper combines with one half of its own weight of sulphur, and the excess of either element above these proportions is discarded. Again, in a mixture however homogeneous, we can generally, by mechanical means alone, distinguish the ingredients. Thus, in the mixture just referred to, a microscope would show the grains of sulphur and metallic copper, with all their characteristic appearances, and by means of carbonic disulphide we can easily dissolve out all the sulphur from the mixture; but after the chemical union has taken place, the characteristic properties of the elements are *merged* in those of the compound, and no such simple mechanical separation is possible. Nevertheless, although these distinctions are generally sufficient, we find in some alloys, in solutions, and in compounds of a few other classes, less intimate conditions of chemical union where these criterions fail.

8. **Chemical Processes.** — The law of definite proportions has a still wider application than that indicated in the last two sections. The chief feature of every well-defined chemical process is, that from one or more definite substances certain other equally definite substances are formed. Thus, in the example just given, from the well-known substances copper and sulphur a new and equally definite substance, cupric sulphide, results. Again, by heating common salt with sulphuric acid, we obtain two other definite substances, hydrosodic sulphate and hydro-

chloric acid gas. So also hydrochloric acid gas and ammonia gas yield ammonic chloride; while chalk and hydrochloric acid give calcic chloride, carbonic dioxide, and water. Now, as in the case of the copper and sulphur, mentioned above, so in all the chemical changes just cited, and in all similar cases, there is a definite relation between the weights of the several substances which take part in or result from the chemical action; and, as will hereafter be shown, we can always calculate the exact proportions in which the required materials should be used, and also the weight of the several products which will result.

9. **Law of Multiple Proportions.** — It is generally the case that the same elements unite in more than one proportion, forming two or more different compounds; and we always find that the proportions of the elements in such compounds are simple multiples of each other. This law is best illustrated by the compounds of nitrogen and oxygen, which are five in number, and have the names indicated in the table below. In order to make evident the law, we give, not the percentage composition as above, but the amount of oxygen, which is in each case combined with one and three fourths parts of nitrogen.

COMPOUNDS OF NITROGEN WITH OXYGEN.

	Nitrogen, by weight.	Oxygen, by weight.	Nitrogen, by volume.	Oxygen, by volume.
Nitrogen Monoxide,	1.75	1	2	1
Nitrogen Dioxide,	1.75	2	2	2
Nitrogen Trioxide,	1.75	3	2	3
Nitrogen Tetroxide,	1.75	4	2	4
Nitrogen Pentoxide,	1.75	5	2	5

So also

	Carbon, by weight.	Oxygen, by weight.
Carbon Monoxide,	3	4
Carbon Dioxide,	3	8

and likewise

	Manganese, by weight.	Chlorine, by weight.
Manganous Chloride,	55	$71.0 = 2\ (35.5)$
Manganic Sesquichloride,	55	$106.5 = 3\ (35.5)$
Manganic Tetrachloride,	55	$142.0 = 4\ (35.5)$

CHAPTER III.

MOLECULES.

10. **Molecular Theory.** — The only explanation of the laws of definite and multiple proportions which up to this time the science of chemistry has furnished, is that all masses of matter have a certain minute granular structure; and that, while there are as many kinds of grains as there are different substances in nature, all the grains of the same substance are alike in every respect. These grains are called molecules, and *are the smallest masses into which a substance can be divided without destroying its identity.*

But while molecules are the smallest particles of *any substance* which can exist by themselves, they must in their turn be regarded as aggregates of still smaller masses of one or more of the seventy chemical elements; and these ultimate *elementary* particles, the smallest masses of matter which science has yet distinguished, are called atoms. The molecules are *the ultimate particles of any substance in which its qualities inhere*, and this is as true of an elementary as it is of a compound substance. But while the molecules of a compound substance are always aggregates of two or more kinds of atoms, the molecules of an elementary substance are aggregates of atoms of the same kind, and in some cases — as, for example, the molecules of mercury and zinc — consist of only one atom (or, in other words, are identical with the atoms).

So long as, in spite of mechanical subdivision or physical changes, the integrity of the molecules is preserved, the identity of a substance remains; but when in a chemical process new substances are formed, the molecules are subdivided and the atoms rearranged to form the new molecules of the resulting product. Thus a lump of sugar is an aggregate of sugar mole-

cules. When dissolved in water, the molecules probably become isolated and distributed among the molecules of the liquid, but the qualities of the sugar are not lost, because the individual molecules remain unchanged. But when the sugar is burnt, the molecules are subdivided, and the resulting atoms of carbon, hydrogen, and oxygen unite to form the molecules of the charcoal, water, and other products which result. In like manner, a drop of water is an aggregate of molecules of water. When converted into steam we still recognize in this vapor the same chemical substance as before, because the molecules, although driven apart by the action of heat, are not otherwise altered. But on passing a current of electricity through the drop, these molecules are subdivided into atoms of oxygen and hydrogen, which unite in pairs — two oxygen atoms together and two hydrogen atoms together — to form the molecules of the oxygen and hydrogen gases which are the products of the electrolysis.

11. **Physical Properties of Matter.** — The physical qualities of a body depend on the relations of its molecules, and the doctrine of molecular structure is even more important as a theory of Physics than it is in Chemistry. The molecules are the units of the physicist, and the points of application of the forces which he chiefly studies. Some of the phenomena he has discovered have enabled him to form approximate estimates of molecular magnitudes, and definite conceptions of the modes of molecular motion; and thus within a few years has arisen a new department of his science, called molecular mechanics.

Solid. — In a solid the molecules firmly cohere, and the force which binds them together has been called *cohesion.* Hence solids have a definite form and structure, and resist any *shearing stress,* or other force which tends to change the relative position of their molecules. Some of the phenomena of crystallization indicate that cohesion is a polar force allied to magnetism; and the well-known qualities of solid bodies, such as crystalline form, elasticity, tenacity, ductility or malleability, hardness, transparency, diathermancy, refracting power, etc., are all, doubtless, different manifestations of a molecular structure which is held together by some mode of polar force. But we have not yet been

able to acquire any positive knowledge in regard to the details of the molecular structure from which such different qualities result. The molecules of all bodies are supposed to be in motion, but in solids the motion is so circumscribed that the relative position of the molecules is not as a rule permanently altered.

Liquid. — In the liquid condition of matter the molecules have great freedom of motion among themselves, and do not resist the least sheering stress; but still the motion is circumscribed within the liquid mass. Hence a liquid has a definite surface, which at each point is at right angles to the direction of the resultant of all the forces acting at that point. Thus the surface of still water is at right angles to the direction of the force of gravitation, and a mass of liquid in equilibrium, like the raindrop, takes a spherical form. In a liquid, however, a certain cohesion still exists between the molecules, and the various phases of capillary action are effects of the *cohesion* of the liquid molecules modified by their *adhesion* to the surfaces of solids. The solvent power of liquids seems to be a still further effect of the same mutual action. Connected also with this freedom of molecular motion is the property of liquids of transmitting pressure in all directions, as are also the well-known principles of hydrostatics to which it leads; but this property belongs to the third condition of matter as well.

Gas. — In the aeriform condition of matter, the motion of the molecules is only circumscribed by the walls of the containing vessel, or by some force acting on the mass from without, in the case of the atmosphere by the force of gravitation. The molecules of a gas are constantly beating against the walls which confine them, and were they not restrained would fly off into space. Hence gases always exert pressure against any surface with which they are in contact, and we measure the pressure, or, as we frequently call it, the *tension* of the gas, by the height to which it will raise a column of mercury (Chem. Phys. 158). The instrument used for this purpose is called a barometer. The height of the barometer, or of any mercury column which represents the pressure or tension of a gas, is always represented by *H*.

In our latitude, at the surface of the sea, the atmosphere in

its normal conditions will raise a column of mercury 76 c. m. high. Hence $H = 76$, and to this standard we always refer in comparing together the volumes of different gases.

12. **Mariotte's Law.** — The most characteristic feature of the aeriform condition is the great change of volume which gases undergo under varying pressure, and the special law of compressibility which they obey. If we represent by H and H' two conditions of pressure to which the *same body* of gas is at different times exposed, then the law is expressed by the formula

$$V : V' = H' : H. \qquad [4]$$

Moreover, since the density, or specific gravity, of a *given mass* of gas must be the greater the less its volume, it is also true that

$$\delta : \delta' = Sp.\ Gr. : Sp.\ Gr.' = H : H'; \qquad [5]$$

and lastly, since the weight of a *given volume* of gas is obviously proportional to its specific gravity, we also have

$$W : W' = H : H', \qquad [6]$$

in which W and W' represent the weight of an *equal volume* of the same gas under the two pressures H and H'.

It must be noticed that in [4] the mass of the gas is assumed to be constant while its volume varies, as is the case when a mass of gas is kept over a pneumatic trough or in an india-rubber bag. On the other hand, in [6] the volume is assumed to be constant while the mass varies, as is the case with the air contained in an open glass bottle or displaced by a glass globe, while [5] is independent either of a constant mass or of a constant volume.

The law of Mariotte may be directly deduced from the theory stated in the last section. For if the molecules of a gas move freely, and gas tension is the effect of an incessant molecular bombardment, it is evident that each of the molecules confined in a given space (a glass globe, for example) must in the long run do the same amount of work. Hence the tension must be proportional to the number of the molecules present, or, what amounts to the same thing, to the density, or specific gravity, of the confined gas. Thus we at once deduce the truth expressed

by [5], and from this proportion we easily pass to [4] or [6], which are the more common, although less simple, expressions of the law.

Temperature is that variable condition of matter whose degrees we roughly designate by the words *hot* and *cold*. The sense of touch gives us the first conception, as well as a rude measure, of temperature, and the thermometer (a familiar instrument, fully described in Chem. Phys. 217–228) is a more accurate measure of the same condition. Experience teaches that there is a constant tendency in nature to an equilibrium of temperature. A cold body brought into a warm room soon becomes warm, and a warm body in a cold room soon falls to the temperature of the surrounding objects. In either case, if there is not an active cause of disturbance, all the objects in the room will soon come to a thermal equilibrium, and a thermometer will show that they all have the same temperature. If a thermometer indicates that two bodies have the same temperature, no thermal change results when they are brought together; but if one is hotter than the other, a change begins at once, and continues until both come to a common temperature. This change is accompanied by the transfer from the hotter to the colder body of a *mode of energy* which we call *heat*.

13. **Heat a Manifestation of Molecular Motion.** — The phenomena of heat, like those of gas tension, are supposed to be merely manifestations of the motion of the molecules of bodies. As the greater the moving power of the molecules, the greater the tension, so also the more intense is the sensation of heat produced. Since temperature is the condition of matter which produces this sensation, it follows that, the greater the moving power of the molecules, the higher the temperature; the less the moving power, the lower the temperature. Moreover, since by the very definition all molecules at the *same temperature* are in the condition to produce the *same sensation* of heat, we must assume further that, whatever their size or weight, they must all have at the same temperature the same moving power. The light molecule of hydrogen must move much faster than the heavy molecule of carbonic anhydride in order to produce the

same effect. If, now, we represent the mass of any molecule by m, and by V its velocity at any given temperature, then the moving power will be represented by $\frac{1}{2} m V^2$ (Chem. Phys. 42), and this will have the same value for every molecule at the same temperature. With a few exceptions, all bodies expand with an increasing temperature, and in the case of mercury the change of volume is so nearly proportional to the change of temperature that we may use the varying volume of a confined mass of this liquid as a measure of temperature. This is the simple theory of the common mercurial thermometer, and in this book we shall refer all temperatures to the degrees of the centigrade scale. These degrees are purely arbitrary; but to each one corresponds a definite value of $\frac{1}{2} m V^2$, and, to a limited extent, we have been able to connect our arbitrary with our theoretical measure.

As in any mass of matter, even when in a constant condition of temperature, there must be, according to the molecular theory, a never ceasing encounter between the numberless moving molecules, we do not suppose that all the individual molecules in such a body have necessarily the same velocity. As in the collision of billiard balls, there must be a constant transfer of velocity; some molecules for the moment coming to rest, while others acquire a very great speed. But so long as no heat is lost or gained, we assume that the transfer of moving power is limited to the molecules of which the body in question consists; and hence, so long as the temperature is constant, the mean velocity of the molecules of a body undergoes no change. When we increase the temperature of the body we must increase this mean velocity, and the total increase of moving power thus acquired is the legitimate measure of the amount of heat which the body receives. Therefore, if we represent by V the mean velocity of the molecules of a body in a given condition, then $\frac{1}{2} m V^2$ represents its temperature, and the sum of the moving powers of all the molecules, or $\Sigma \frac{1}{2} m V^2$, the whole amount of heat which it contains.

Practically, however, we measure quantity of heat by an arbitrary standard, and we shall use in this book as our unit the amount of heat required to raise the temperature of a kilo-

gramme of pure water from 0° to 1° centigrade. This we call the *unit of heat*, and it has been found, by careful experiments, that this unit of heat represents an amount of moving power which is adequate to raise a weight of 423 kilogrammes one metre, or to do any other equivalent amount of work.

14. **Expansion by Heat.** — The amount of expansion which bodies undergo when heated has been carefully measured for many different substances, and the results are tabulated in most works on physics (Chem. Phys., Table XV.). The so-called coefficient of expansion given in these tables is the small fraction of its volume, taken at 0° C., which a body increases when heated one centigrade degree. If, now, k represents this fraction, V the initial volume, V' the new volume, t the initial temperature, and t' the new temperature, then, if we assume that the expansion is proportional to the temperature, we easily deduce the formula (Chem. Phys. 239),

$$V' = V[1 + k(t' - t)]. \qquad [7]$$

This formula serves to calculate, with sufficient accuracy for most purposes, the change of volume of solids, whose coefficients of expansion are very small fractions and whose rates of expansion are nearly uniform. The same, however, is not true of liquids, whose rates of expansion frequently increase with the temperature very rapidly; and for such bodies we are obliged to use the following formula, which is much less simple, but is of the general form in which every algebraic function may be developed: —

$$V' = V(1 + At + Bt^2 + Ct^3 + \text{etc.}). \qquad [8]$$

In this formula, V' represents the required volume at some temperature, t, and V the volume at 0°, which is assumed to be known; while A, B, C, etc. are numerical constants, which have been determined by experiment in the case of most liquids (Chem. Phys. 255).

But while every solid or liquid has its own rate and law of expansion, which may be empirically expressed in the manner we have just described, it is quite different with aeriform matter. All gases have very nearly the same rate of expansion, and, more-

over, the amount of expansion is always closely proportional to the increase of temperature.

These relations would probably hold absolutely if all gases exactly obeyed Mariotte's law, and realized the condition which we regard as that of a perfect gas. But as no known aeriform substances are perfect gases, we can discover by delicate experiments slight differences in their rates of expansion. Still, except in the case of vapors near their point of condensation, and in the case of a few gases, which are very easily condensed, the differences may be disregarded in all chemical problems.

Both solids and liquids expand with irresistible force, and we have therefore only this one effect to consider in regard to the action of heat upon them. It is different, however, with gases. By enclosing a gas in a tight vessel we can raise its temperature without changing its volume, except so far as the vessel itself becomes enlarged by heat. The effect of the heat is, then, to increase the tension or pressure exerted by the gas. Hence, in the case of a gas, we may have two distinct effects: first, an increase of volume when the pressure is constant; secondly, an increase of tension when the volume is constant.

Studying, in the first place, the last effect, we discover this very simple law, which holds for all forms of aeriform matter in so far as they obey Mariotte's law. A confined mass of gas under constant volume gains or loses $\frac{1}{273}$ of its tension at 0° C. for a gain or loss of temperature of one degree at any point on the centigrade scale. Assuming that we start with a confined mass of air, or of any other equally perfect gas, having a tension of 273 m. m. at 0°, the tension would increase or diminish exactly one millimetre for a rise or fall of temperature of one degree. At +273° the tension would be 546 m. m., or just double; and if the law holds to the extreme limits it would be reduced to nothing at −273°. Although the law has not been verified for low temperatures except to a very limited extent, it is convenient to assume that this point, where molecular motion theoretically ceases, is the absolute zero of the thermometer scale. Representing then by t_0 and t'_0, two absolute temperatures obtained by simply adding 273 to the temperatures expressed on the centigrade scale,

we obtain this simple expression of what is known as the law of Charles:—

$$H : H' = t_0 : t'_0 \qquad [9]$$

Moreover, since on allowing the confined gas to expand or contract under the pressure of the atmosphere — assumed to be constant — the resulting volume would be directly as the initial tension, we deduce by comparison with [4],

$$V : V' = t_0 : t'_0 \qquad [10]$$

Variations of temperature produce such important changes in the volume and specific gravity of all bodies, and especially of gases, that it becomes frequently essential, before comparing different observations, to reduce them all to some standard temperature. Most scientific men use, as this standard temperature, 0° centigrade, and scientific measures are generally adjusted to this standard; but 60° Fahrenheit, corresponding to 15°.5 centigrade, is often a more convenient standard, because it is nearer the mean temperature of the air, and is, therefore, not unfrequently employed.

From [4] and [10] we can deduce the following simple formula, by which such reductions are easily made:—

$$V' = V \frac{H}{H'} \cdot \frac{t'_0}{t_0}. \qquad [11]$$

In this expression the mass of the gas is assumed to be constant, while the volume varies with the change of temperature or pressure. But in the same way we can deduce from [6] the similar formula:—

$$W' = W \frac{H'}{H} \cdot \frac{t_0}{t'_0}, \qquad [12]$$

in which the volume is assumed to be constant and the mass to vary.

In using these formulæ confusion will be avoided if the student asks himself in each case whether the initial volume or weight is increased or lessened by the change of temperature or pressure, and then places in the numerator of the fraction the greater or the smaller of the two temperatures given, or of the two pressures given, as the conditions indicate.

In measuring or weighing aeriform matter the ordinary cases with which we have to deal are, first, those in which the volume of a constant mass (for example, a volume of gas confined in a bell over a pneumatic trough) varies with a varying temperature or pressure, and, secondly, those in which the weight of a constant volume but changing mass (for example, the weight of air displaced by a glass globe) varies from the same causes. In the proportion

$$V : V' = H' : H = t_0 : t'_0$$

we assume the first of these conditions, and in

$$W' : W = t_0 : t'_0 = H' : H$$

we assume the second. By combining these proportions we can deduce

$$\frac{VW'}{V'W} = \frac{Ht_0}{Ht'_0},$$

an expression in which either the volume or the weight may be regarded as the variable, as the case requires, and which exhibits all the relations of the several quantities.

15. **Change of State.** — Many substances are capable of existing in all the three conditions of matter. Now, we find that whenever a solid changes to a liquid, or a liquid to a gas, heat is absorbed; and conversely, whenever a gas is liquefied, or a liquid becomes a solid, heat is evolved; although, as a general rule, this change of state is accompanied by no change of temperature. Thus, one kilogramme of ice, in melting, absorbs 79 units of heat, although the temperature remains at 0° during the change; and when, by boiling, a kilogramme of water is converted into steam, under the normal pressure of the air, no less than 537 units of heat disappear, although the temperature both of the steam and of the water is constant at 100° during the whole period. On the other hand, when the steam is condensed or the water frozen, absolutely the same amount of heat is set free as was before absorbed. The heat thus absorbed or set free is generally called the *latent heat* of the liquid or gas, and in the case of many substances the amount has been carefully meas-

ured (Chem. Phys. 277 and 299). According to the theory we are studying, these effects are the direct results of the molecular condition of matter. The change of state must be accompanied by a change in the relative position of the molecules, or in their mean distance from each other; and this change, in its turn, must be attended with a destruction or production of the moving power on which the effects of heat depend (Chem. Phys. 215 *bis*).

16. **Sources of Heat.** — The sun is the original source of almost all the heat we enjoy on the earth, for the effect of the earth's internal heat, at its surface, is at best very small, and all our artificial sources of heat have drawn their supply either directly or indirectly from the great central luminary. According to our theory, the effect of the sun's rays is a simple result of the transfer of molecular motion from the sun to the earth, either by some unknown influence exerted from a distance, or else by an actual transfer of motion through the material particles of the ether which is assumed to fill the intervening space. The great source of all artificial heat is combustion in its many forms, and this, as we shall hereafter see, is merely a clashing together of material molecules, and is necessarily attended with a great development of that moving power to which we refer all thermal effects.

17. **Specific Heat.** — The amount of heat required to raise to the same extent the temperature of equal weights of different substances is by no means the same. This quantity is capable in any case of exact measurement, and is called the specific heat of the substance. The amount of heat required to raise the temperature of one kilogramme of water one centigrade degree has been assumed as the unit, and we express the specific heat of other substances in terms of this measure. Moreover, since with very few exceptions the specific heat of water is greater than that of any substance known, the specific heat of all other bodies is to be expressed by fractional numbers. In every case, unless otherwise stated, the numbers indicate what fraction of a unit of heat would be required to raise the temperature of one kilogramme of the substance from 0° to 1° centigrade (Chem. Phys. 232).

18. **Molecular Condition of Gases.** — The aeriform state is by far the simplest condition of matter, and the two peculiarities in its properties which we have studied lead to important conclusions in regard to its molecular conditions. These characteristics are as follows: first, all true gases obey the same law of compressibility; secondly, equal volumes of all true gases expand equally on the same increase of temperature (§§ 12 and 14). Now, according to the theory of molecular mechanics, these peculiar relations of the aeriform condition of matter can only be explained on the assumption that *equal volumes of all gases contain the same number of molecules;* and this important theoretical deduction — which is usually known as the law of Avogadro — lies at the basis of our modern theories of chemistry. This peculiar molecular condition, however, is only found in the gas, for it is only in this state that the molecules are sufficiently separated from each other to be freed from the mutual action of those molecular forces which give rise to far more complicated relations in both liquid and solid bodies. Moreover, with our ordinary gases (in the degree of condensation in which they exist under the pressure of the atmosphere) the molecules are not yet sufficiently far apart to be wholly freed from the effects of their mutual action, and hence the theoretical condition is not absolutely fulfilled; and in vapors, where the molecules are still closer together, the variation from the theory is sometimes quite large. In proportion as the gas expands, the theoretical condition is approached, and, when in a state of great expansion, equal volumes of all gases would undoubtedly contain exactly the same number of molecules. It is only then that we reach the condition of what we have called above the perfect *gas*, and our criterion of this perfect state is, that the gas then obeys absolutely the law of Mariotte. A very important corollary follows at once from the principle we have just deduced: —

The molecular weight of all substances is directly proportioned to their specific gravities in the state of perfect gas.

We have adopted in this book hydrogen gas as our unit of specific gravity for aeriform substances, and were we also to take

the molecule of hydrogen as our unit of molecular weight, then the number which expresses the specific gravity of a gas would express also its molecular weight. But, for reasons which will appear hereafter, we have selected the half-molecule of hydrogen as our unit, and hence *the molecular weight of any substance in terms of this unit is always twice its specific gravity in the state of gas.* In Table III. we have given, according to the most accurate experimental data, the Sp. Gr. (referred to hydrogen) of all the best-known gases and vapors, and in a parallel column we have also given the half molecular weights of the same substances determined by chemical analysis, in a manner which will be hereafter described. It will be seen that the numbers in the second column are almost precisely the same as those in the first; and the slight differences which will be noticed either arise from the fact that the vapors, under the conditions in which alone their Sp. Gr. can be accurately determined, are not true gases, that is, do not exactly obey Mariotte's law, or else, where the differences are more considerable, may be referred to a partial decomposition of the substance itself in the process of the experiment. In solving the problems of this book, and generally in most chemical problems, the half-molecular weight may be taken as the true Sp. Gr. The logarithms of these values given in the last column of the table will be found useful in this connection. Although only given to four places of decimals, they exceed in accuracy the experimental data. The values in the column of **Sp. Gr.** referred to air are given, as a rule, to one decimal place beyond the limit of error.

It will perhaps serve to give greater definiteness to our conceptions if, even at the risk of coining a new word, we call the unit of molecular weights a *microcrith.* We have already become familiar with the crith, the weight of one litre of hydrogen; and our new unit of weight, the *microcrith*, is the weight of the half-molecule of hydrogen, and although a unit of a very different order of magnitude, as its name implies, the microcrith is just as real a weight as the crith or the gramme. Remembering, then, that the weight of one half of a hydrogen molecule is a microcrith, it is evident that a molecule of hydrogen gas weighs two micro-

criths (2 m. c.). The Sp. Gr. of oxygen gas being 16, the molecule of oxygen gas must weigh sixteen times as much as the molecule of hydrogen gas, that is, it must weigh 32 m. c. In like manner, the Sp. Gr. of aqueous vapor being 9, and that of alcohol vapor 23, the molecules of water and alcohol must weigh 18 m. c. and 46 m. c. respectively. According to the estimates of the late Professor Clerk Maxwell, the microcrith is 33×10^{-25} of a gramme. This he regarded, however, as only a very rough approximation; and our only object in giving such a rude estimate in this connection is to persuade the reader that in the modern theory of chemistry the microcrith is as real a value as the gramme. Here, as elsewhere in science, we measure magnitudes by units of the same order. We can seldom determine with precision the relation between units of such an utterly different order as a microcrith and a gramme; but chemistry has given us the means of determining the weight of molecules in microcriths with as much accuracy as we can determine the weight of palpable objects in grammes.

We have said that the half-molecular weights of Table III. were determined by chemical analysis, and it has appeared that, however striking the general agreement, the molecular weights thus determined seldom exactly agree with those deduced from the specific gravities of the several substances in the state of gas or vapor. The student cannot expect, until more advanced, to comprehend all the bearings of the subject, but the following considerations may make the relations of these two values more intelligible.

Remembering that the molecule is the smallest mass of any substance in which its qualities inhere, and therefore that in a chemical process the action must take place between the molecules of the substances involved, — one or more molecules of one substance reacting on a definite number of molecules of each of the other substances, and yielding a definite number of molecules of the several products which are formed, — it will easily be seen that the definite proportions which obtain in such cases (§ 8) are simply the relations between the weights of the molecules involved in the change. Now, in most cases, the processes of

chemical analysis give us the means of determining the definite proportions which obtain in any given chemical process with great precision; but they do not give us the means of discovering with equal certainty whether these definite proportions stand for the relative weight of one or of several molecules of the substances involved. But exactly this information the specific gravities of the substances in the condition of gas or vapor supply. These we know are to each other as the weights of single molecules, and although, for the reasons we have referred to, this relation is not precise, it is near enough to enable us to interpret our more accurate analytical results, and to decide whether they are the proportions of single molecules or the multiples of these proportions. Thus, while theoretically the determination of molecular weights is based on the comparison of the weights of equal gas volumes, practically this comparison only gives an approximation to the truth, and we depend on the method of chemical analysis for fixing the precise value. Moreover, it is evident that the theoretical method of determining molecular weight is only applicable to those substances which are capable of existing in the aeriform condition. The greater number of chemical compounds cannot be volatilized without decomposition. In all such cases we must depend entirely on chemical methods for fixing the molecular weight, and sometimes we cannot be certain whether the weight we assign to the molecule of a non-volatile substance is the true value or some simple multiple of this value. Generally, however, — as will be shown hereafter, — the chemical relations of the substance give the means of deciding this question.

QUESTIONS AND PROBLEMS.

1. Are the qualities of a molecule of any substance the same as those which distinguish the substance itself?

2. What is the distinction between cohesion and adhesion?

3. When the barometer stands at 76 c. m., with what weight in grammes is the air pressing against each square centimetre of surface? *Sp. Gr.* of mercury 13.596. Ans. 1033.

4. To what difference of pressure does a difference of one centimetre in the barometric column correspond? Ans. 13.596 grammes.

5. When a mercury barometer stands at 76 c. m., how high would a water barometer stand? Also, how high would barometers stand filled with alcohol or sulphuric acid, disregarding in each case the tension of the vapor? *Sp. Gr.* of alcohol 0.81; *Sp. Gr.* of sulphuric acid 1.85. Ans. 1,033; 1,275 and 558.2 c. m.

6. A volume of hydrogen gas was found to be 200 $\overline{\text{c. m.}}^3$ The height of the barometer observed at the same time was 74 c. m. What would have been the volume if observed when the barometer stood at 76 c. m.? Ans. 194.7 $\overline{\text{c. m.}}^3$

7. A volume of nitrogen standing in a bell-glass over a mercury pneumatic trough measured 250 $\overline{\text{c. m.}}^3$ The barometer at the time stood at 75.4 c. m., and the level of the mercury in the bell was found by measurement to be 6.5 c. m. above the surface of the mercury in the trough. Required to reduce the volume to standard pressure.

Ans. The pressure of the air on the surface of the mercury in the trough (measured at 75.4 c. m.) was balanced first by the column of mercury in the bell, and secondly by the tension of the confined gas. Hence the pressure to which the gas was exposed was equal to $75.4 - 6.5 = 68.9$ c. m., and we have $76 : 68.9 = 250 : x = 226.7$ $\overline{\text{c. m.}}^3$

8. What would be the answer to the same problem, had the trough been filled with water?

Ans. The water column in the bell exerts a pressure which is as much less than the pressure of the mercury column in the previous problem as the *Sp. Gr.* of water is less than the *Sp. Gr.* of mercury. Hence we have $13.6 : 1 = 6.5 : 0.48$; also, $75.4 - 0.48 = 74.92$, and $76 : 74.92 = 250 : x = 246.4$ $\overline{\text{c. m.}}^3$

9. A closed vessel, which displaces one litre of air, is poised on a balance with weights, whose volume is inconsiderable when compared with that of the vessel. The balance is in equilibrium when the barometer stands at 76 c. m. If the barometer falls to 73 c. m., how much weight must be added to restore the equilibrium? The temperature is assumed to be constant and at 0° C. Ans. 85 milligrammes.

10. Given the weight of one litre of dry air under the normal conditions as 14.43 criths, what will be the weight of one litre of dry air at the normal temperature, but under a pressure of 72 c. m.?

Ans. 13.68 criths.

11. A volume of gas measures 500 $\overline{\text{c. m.}}^3$ at 15°; what will be its volume at 303°? In this and the next three problems the pressure is assumed to be constant. Ans. 1,000 $\overline{\text{c. m.}}^3$

12. To what temperature must an open vessel be heated before one quarter of the air which it contains at 0° is driven out? Ans. 91°.

13. An open vessel is heated to 819°. What portion of the air which the vessel contained at 0° remains in it at this temperature?

Ans. $\frac{1}{4}$.

14. A closed glass vessel, which at 13° was filled with air having a tension of 76 c. m., is heated to 585°. Determine the tension of the heated air. Ans. 3 atmospheres.

15. Reduce the following volumes of gas, measured at the temperatures and pressure annexed, to 0° and 76 c. m.

1. 140° $\overline{\text{c. m.}}^3$ $H = 57$ c. m. $t = 136°.5$ Ans. 70 $\overline{\text{c. m.}}^3$
2. 320° $\overline{\text{c. m.}}^3$ $H = 95$ c. m. $t = 91°$ Ans. 300 $\overline{\text{c. m.}}^3$
3. 480° $\overline{\text{c. m.}}^3$ $H = 38$ c. m. $t = 68°.25$ Ans. 192 $\overline{\text{c. m.}}^3$

16. What is the weight of dry air contained in a glass globe of 640 $\overline{\text{c. m.}}^3$ capacity, at the temperature 546° and under a pressure of 71.25 c. m.? Ans. 0.2586 gramme.

General Solution. — In order to make the solution general we will represent the capacity of the globe, the temperature, and the tension of the air by V, t, and H respectively. We can also easily find from Table III. that one cubic centimetre of dry air weighs 0.01443 crith, or 0.001293 gramme, when $H = 76$ c. m. and $t° = 0$. The weight of V cubic centimetres of dry air at any other temperature and tension is then at once deduced from [13],

$$W = 0.001293 \frac{H}{76} \cdot \frac{273}{273 + t} \cdot V. \qquad [13]$$

We must next take into consideration the change of capacity of the glass globe due to the change of temperature. This causes no sensible error when the change of temperature is small, but when the change is large its effect must be considered. If the capacity is V $\overline{\text{c. m.}}^3$ at 0°, at $t°$ it becomes V $(1 + t\, 0.000025)$, at least very nearly for ordinary glass [7]. Introducing this value for V into the above equation, we obtain

$$W = 0.001293 \frac{H}{76} \cdot \frac{273}{273 + t} V (1 + t\, 0.000025). \qquad [14]$$

The corresponding weight of pure dry hydrogen gas may also be found by the same formula, only in that case 0.0000896 must be substituted for 0.001293.

To facilitate calculation by logarithms, the formula may be easily brought into the following form:—

$$\left.\begin{array}{l}\text{For air}\\ W = 7.6670\\ \text{For hydrogen}\\ W = 6.5077\end{array}\right\} + \log. H + \text{ar. co. log. } (273 + t) + \log. V + \log. (1 + t\, 0.000025). \quad [15]$$

17. To find the **Sp. Gr.** of a vapor by Dumas's method.

Solution. — The specific gravity of a vapor has been defined as its weight compared with the weight of the same volume of hydrogen gas under the same conditions of temperature and pressure; but practically it is most convenient to determine the specific gravity with reference to air, and subsequently to reduce the result to the hydrogen standard.

To find, then, the **Sp. Gr.** of a vapor, we must ascertain the weight of a known volume, V, at a known temperature, t, and under a known pressure, H, and divide this by the weight of the same volume of air at the same temperature and under the same pressure. The method may best be explained by an example. Suppose, then, that we wish to ascertain the **Sp. Gr.** of alcohol vapor. We take a light glass globe having a capacity of from 400 to 500 c. m.^{3}, and draw the neck out in the flame of a blast lamp, so as to leave only a fine opening, as shown in the figure at a. We then weigh the globe, setting it on the balance pan with its mouth open. This gives us the weight of the glass, which we will represent by W. The second step is to ascertain the weight of the globe filled with alcohol vapor at a known temperature and under a known pressure. For this purpose we introduce into the globe a few grammes of pure alcohol, and mount it on the support represented in the accompanying figure. By loosening the screw, r, we next sink the balloon beneath the oil contained in the iron vessel, V, and secure it in this position. We now slowly raise the temperature of

the oil to between 300° and 400°, which we observe by means of the thermometer, T. The alcohol changes to vapor, and drives out the air, which, with the excess of vapor, escapes at a. When the bath has attained the requisite temperature, we close the opening a, by suddenly melting the end of the tube at a with a mouth blowpipe, and as nearly as possible at the same moment observe the temperature of the bath and the height of the barometer. Let us represent the temperature and tension of the vapor at the moment the globe was sealed by t' and H'. We have now in the globe an amount of alcohol whose vapor just filled the interior under these conditions, and since the globe is hermetically sealed, its weight cannot change, and we can therefore allow it to cool, clean it, and weigh it at our leisure. Evidently, however, the apparent weight of the glass and alcohol shown by the balance is not the true weight, because the globe is buoyed up by the air it displaces. The next step, therefore, is to find the weight of this air, and in order to do this we must know the volume of the globe and also the temperature and pressure of the air in the balance case at the time the weight was taken. This temperature t and this pressure H having been observed, to find the volume of the globe we break off the tip of the tube (a) under distilled water, which has been previously boiled, and cooled in a tightly corked flask, in order to prevent the formation of air-bubbles; the weight of the globe filled with water is next found in grammes on a coarse balance, and subtracting from this weight the known weight (W) of the glass, we have, in cubic centimetres, the volume of the interior of the globe. Represent this by V. Having now the data V, H, and t, we find from [13] the weight of the air displaced by the globe less that displaced by the glass. Of the last it is not necessary to take account, as it is to a great extent compensated by the displacement of the brass weights. If we call the weight of the displaced air W'', then the weight of the alcohol whose vapor filled the balloon at t' and H' was W' (apparent weight of globe and alcohol) + W'' (weight of air displaced) − W (weight of glass). It only remains now to find by [14] the weight of an equal volume of air at the same temperature and pressure, taking into account, of course, the increased volume of the globe at the high temperature. Representing this last weight by W''', we have finally,

$$\text{Sp. Gr.} = \frac{W' + W'' - W}{W'''}.$$

1st. Ascertain the **Sp. Gr.** of alcohol vapor from the following data : —

Weight of glass globe,	W	50.804	grammes.
Height of barometer,	H	74.75	centimetres.
Temperature,	t	18°	
Weight of globe and vapor,	W′	50.824	grammes.
Height of barometer,	H′	74.76	centimetres.
Temperature,	t'	167°	
Volume,	V	351.5	cubic centimetres.

The calculation may take the following form : —

For W″.			For W‴.	
Constant log.		7.6670		7.6670
H = 74.75 log.		1.8736	H′ = 74.76 log.	1.8737
273 + t = 291 ar. co.		7.5361	273 + t' = 440 ar. co. log.	7.3565
V = 351.5 log.		2.5459		2.5459
W″	0.4194	9.6226	(1 + 167 × 0.000025) log.	0.0017
W′	50.824		W‴ log.	9.4448
W″ + W′	51.2434		(W″ + W′ − W) log.	9.6429
W	50.804			
W″ + W′ − W	0.4394		**Sp. Gr.** = 1.578	0.1981

2d. Ascertain the **Sp. Gr.** of camphor vapor from the following data : —

Weight of glass globe,	W	50.134	grammes.
Height of barometer,	H	74.2	centimetres.
Temperature,	t	13°.5	
Weight of globe and vapor,	W′	50.842	grammes.
Height of barometer,	H′	74.2	centimetres.
Temperature,	t'	244°	
Volume,*	V	295	cubic centimetres.

Ans. 5.372.

* On filling the globe with water in the manner above described, it usually happens that a small bubble appears, showing that the air was not completely expelled by the vapor. If the volume of this bubble is more than one or two cubic centimetres, the amount should be measured, and the value of V diminished by the volume which the bubble must have had at the time of sealing the globe; for it is evident that the available volume of the globe was lessened by this amount. Since now we have given t' and H′ and can observe t and H, — the temperature and pressure at which the small residual volume of air is measured, — we can easily calculate by [11] the correction required; and this must be sub-

18. To find the specific gravity of a vapor by Hofmann's method.

In this method we observe the volume and tension of the vapor which a weighed amount of substance forms at a definite temperature.

It is then easy to calculate by [14] the weight of an equal volume of air under the same conditions.

The apparatus consists of a wide barometer tube about a metre long, and graduated into cubic centimetres. This tube is filled with mercury, and inverted over a mercury cistern, as in the experiment of Torricelli. The mercury sinks of course to the height of about 76 centimetres, leaving a vacuous space at the top of the tube. Around the barometer tube is adjusted, by means of a rubber stopper, a somewhat larger tube, also of glass, which serves as a jacket, and

through this is passed steam (or the vapor of a liquid boiling at a higher temperature than water) in order to heat the apparatus to a constant and known temperature. The apparatus having been arranged as represented in our figure, — with a cathetometer for measuring the height of the mercury column at its side, — a few decigrammes of substance are weighed out as accurately as possible in a very small glass-stoppered bottle, which is then passed under the mercury into the barometer tube. The bottle at once rises into the vacuous space, when the volatile substance, expanding with the heat and forcing out the stopper, evaporates into the space above the mercury, and depresses the column.

tracted from the total cubic contents of the globe to obtain the value of V which is to be used in the above calculations. The correction, however, is somewhat uncertain, and should be avoided as far as possible by adapting the size of the globe to the quantity of liquid which is available for the determination, and avoiding any fluctuations in the temperature of the bath by which air might be drawn back into the globe.

We have now a known weight of vapor at a known temperature, and we at once read off the volume by means of the graduations on the barometer tube. It remains only to find its tension; and since this tension, added to the pressure of the column of mercury in the barometer tube of the apparatus, evidently balances the pressure of the atmosphere, the value required can be easily calculated when we know the height of the mercury column.

This height is now measured with the cathetometer, and, after reducing it to 0°,* we subtract the amount from the height of a neighboring barometer reduced in a similar way.

We know now, besides the weight, W, and the volume, V, of the vapor, also its temperature, t, and its tension, H, and we can calculate by [14] the weight of an equal volume of air under the same conditions.

If we call this weight W′, we have

$$\text{Sp. Gr.} = \mathrm{W} \div \mathrm{W}'.$$

19. Required the Sp. Gr. of common ether when in Hofmann's method the tube is heated with free steam. W = 0.2298 gramme. V = 125 c. m.^{3} $\mathrm{H}_0 = 76$. $h_0 = 19$.

Solution. — Constant log.	7.6670
$\mathrm{H}_0 - h_0 = 57$ log.	1.7559
$273 + t = 373$ ar. co. log.	7.4283
V = 125 log.	2.0969
$(1 + 100 \times 0.000025)$ log.	0.0008
	8.9489
W = 0.2300 log.	9.3617
Ans. Sp. Gr. = 2.587	0.4128

20. Required the Sp. Gr. of chloroform vapor, when, as in last example, $t = 100°$ and also W = 0.2500 gramme. V = 110 c. m.^{3} $\mathrm{H}_0 = 75.62$. $h_0 = 32.25$. Ans. Sp. Gr. = 4.20.

* This reduction is calculated by means of the formula $\mathrm{H}_0 = \mathrm{H} - \mathrm{H}\frac{t}{550 + t}$, and the last term is the correction which must be subtracted from the observed height in order to reduce the observations to 0°, that is, to find the height which the column would have had if the temperature of the mercury alone had been zero. The principles involved are explained in Chem. Phys. (251), and in the same work a table is given from which the correction for the barometer may be obtained by inspection. It is assumed that the heights of the barometer given above have been corrected in this way.

21. Find the **Sp. Gr.** of acetic acid vapor, using in Hofmann's method the vapor of boiling aniline, B. P. = 182°, to heat the tube. W = 0.1250 gramme. V = 157 c. m.^{3} $H_0 = 76.80$. $h_0 = 39.60$.

Ans. **Sp. Gr.** = 2.086.

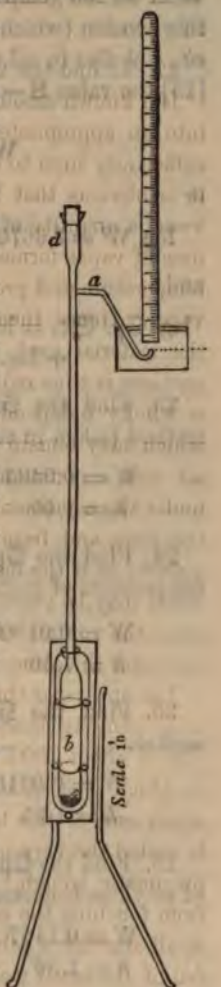
22. To find the **Sp. Gr.** of a vapor by the method of Victor Meyer.

If a known amount of some volatile substance is suddenly dropped into an appropriate vessel, heated to a constant temperature, which is sufficiently high to convert the substance into the aeriform condition, it is obvious that the substance in volatilizing will expel from the vessel a quantity of air which must be the exact equivalent of the volume of vapor formed; that is, an amount of air which at the unknown temperature and pressure in the vessel would just fill the space of the vapor. Hence, then, the **Sp. Gr.** of the vapor is the known weight of the material used, divided by the weight of the air expelled. The problem is thus reduced to finding the weight of the air expelled, and is wholly independent of the temperature and volume of the vessel, which may remain unknown quantities. We have only to collect the air over a common water pneumatic trough, and measure its volume under the conditions of temperature and pressure in the laboratory at the time, and from these data we can easily calculate the weight required; or if the material under examination is liable to oxidation, the vessel may be previously filled with nitrogen or some other inert gas, since the volume of such gas will be the same as the volume of the air under the same circumstances.

The apparatus that may be used in most cases is represented in the accompanying figure, which is drawn to scale. The bulb, *b*, has a capacity of about 100 c. m.^{3} and is about 20 c. m. long, and the glass tube to which it is attached is about 60 c. m. long and 6 m. m. wide. The upper end of this tube is closed by a rubber stopper, while to its side is united the very narrow tube *a*, which conducts the expelled air to a pneumatic trough. By means of a wire guard the bulb is prevented from touching the sides of the iron bath in which it is heated, and a small amount of asbestos at the bottom of the bulb serves to break the fall of the small weighing tube, holding the weighed substance, which is dropped in at *d*. The iron bath is made of a short piece of two-inch gas-pipe, closed by welding at the bottom, and supported on a tripod of such height that, while the tripod stands on the floor, the pneumatic trough may rest on a table of medium height. In the bath may be used paraffine or a molten metal as circumstances require, and its tem-

perature is maintained by gas-burners more or less powerful according to the temperature required. In some later experiments Meyer used a porcelain vessel heated in the muffle of a gas furnace to a temperature between the melting-points of cast-iron and steel.

After the bath has been heated to the degree required, and its temperature has become constant (a condition which is indicated by the fact that bubbles of gas cease to escape from the open mouth of the tube, while at the same time there is no tendency in the water to recede), the necessary observations are made in a very simple way. The stopper at *d* is removed, and the tube containing the weighed substance * dropped in, when instantly the stopper is replaced. The few bubbles of air displaced by the stopper are of course neglected, but the air, which soon begins to stream over in consequence of the volatilization of the material introduced, is collected over water in an ordinary graduated tube. The experiment is soon finished, and the stopper *d* must then be removed to prevent any recession of the water.



It remains only to measure the volume of the air in the graduated tube with the usual precautions. For this purpose the tube is transferred to a cylindrical glass vessel of water, and held by a clamp in a vertical position, so that the water is at the same level within and without the tube; and, as soon as an equilibrium of temperature is attained, we observe, 1. the volume of the air, 2. the temperature of the air (necessarily the same as that of the water confining it), and 3. the height of a neighboring barometer. We have now V, H, and *t*, from which we easily calculate by [13] the corresponding weight of the expelled air. But in making this calculation we must remember that the air when measured is saturated with moisture, and therefore that, in order to find

* The amount of substance taken should not more than half fill the vessel *b* with vapor.

the true tension of the confined air, we must subtract from the reduced height of the barometer the *maximum tension* of the vapor of water at the temperature t (Chem. Phys. 312). Representing by h this tension (which is to be taken from tables found not only at *loc. cit.*, but also in all works on meteorology), and substituting for H in [13] the value $H - h$, we obtain for the weight of the displaced air,

$$W' = 0.001293 \frac{H - h}{76} \cdot \frac{273}{273 + t} V,$$

or

$$\log. W' = 7.6670 + \log. (H - h) + \text{ar. co. log. } (273 + t) + \log. V,$$

and

$$\log. \text{Sp. Gr.} = \log. W - \log. W' = 2.3330 + \text{ar. co. log. } (H - h) + \log. (273 + t) + \text{ar. co. log. } V + \log. W.$$

23. Find the Sp. Gr. of carbonic disulphide vapor by Meyer's method (taken in steam bath).

$W = 0.0495$ $t° = 16.5$ $H = 71.78$ $V = 16.4$
$h = 1.40$ Ans. 2.67.

24. Find the Sp. Gr. of the vapor of arsenious oxide (taken at temperature of molten cast-iron).

$W = 0.0130$ $t° = 15.4$ $H = 72.38$ $V = 17.8$
$h = 1.30$ Ans. 0.64.

25. Find the Sp. Gr. of xylol vapor in a bath of vapor of aniline.

$W = 0.0715$ $t° = 16$ $H = 72.38$ $V = 16.5$
$h = 1.35$ Ans. 3.79.

26. Find the Sp. Gr. of iodine vapor (taken in a bath of the vapor of amylene benzoate).

$W = 0.1157$ $t° = 16.1$ $H = 72.23$ $V = 11.6$
$h = 1.36$ Ans. 8.75.

27. Find the Sp. Gr. of mercury vapor (taken in bath of molten lead).

$W = 0.0905$ $t° = 16$ $H = 71.58$ $V = 11.5$
$h = 1.35$ Ans. 6.97.

28. Find the **Sp. Gr.** of sulphur vapor (taken in a bath of molten lead).

$W = 0.1030$ $t° = 16$ $H = 71.38$ $V = 13.9$
$h = 1.35$ Ans. 6.58.

29. Find the **Sp. Gr.** of sulphur vapor (taken in the muffle of a gas-furnace at temperature above that of molten cast-iron).

$W = 0.0267$ $t° = 16.5$ $H = 72.28$ $V = 10.8$
$h = 1.40$ Ans. 2.17.

30. Find the **Sp. Gr.** of the vapor of arsenious oxide (taken at temperature of molten cast-iron).

$W = 0.1583$ $t° = 15$ $H = 71.78$ $V = 10.1$
$h = 1.27$ Ans. 13.78.

31. It is known that 1 part of hydrogen gas combines with 8 parts of oxygen gas to form 9 parts of water; that 1 part of hydrogen gas combines with 35.5 parts of chlorine gas to form 36.5 parts of hydrochloric acid gas; that 36.5 parts of hydrochloric acid gas combine with 17 parts of ammonia gas to form 53.5 parts of ammonic chloride; that 14 parts of olefiant gas combine with 35.5 parts of chlorine gas to form 49.5 parts of ethylene chloride; that 147.5 parts of chloral combine with 18 parts of water to form 165.5 parts of chloral hydrate. Compare these experimental results with the gas or vapor densities of the same substances, and show that from these data the exact molecular weights of the several substances may be deduced. In making comparison use Table III.

NOTE. — We have not dwelt in this chapter on the correction of gas volumes for the tension of aqueous vapor, because a discussion of the principle involved does not come within the scope of our work. This correction becomes of great importance, however, when a gas volume is measured over water; and it is essential for accuracy that a volume of gas to be measured should either be perfectly dry or else saturated with vapor. If dry, no correction is required; but if saturated with vapor (as the gas will be if it stands for a few minutes in contact with water), the temperature must be carefully observed, and the *maximum tension* of aqueous vapor at the given temperature subtracted from the observed tension to find the true tension of the gas. Tables giving the maximum tension of aqueous vapor at different temperatures will be found in the author's work on Chemical Physics, and in that book (§ 329) this whole subject is fully discussed.

CHAPTER IV.

ATOMS.

19. **Definition.** — As has been already stated, the molecular theory assumes that so long as the identity of a substance is preserved its molecules remain undivided; but when, by some chemical change, its identity is lost, and new substances are formed, the theory supposes that the molecules themselves are broken up into still smaller particles, which it calls *atoms*. Indeed, it regards this division of the molecules as the very essence of a chemical change.

The word "atom" is derived from *α* (privative) and *τέμνω* (I cut), and recalls a famous controversy in regard to the infinite divisibility of matter, which for many centuries divided the philosophers of the world. But chemistry does not deal with this metaphysical question. It asserts nothing in regard to the possible divisibility of matter; but its modern theories claim that, practically, this division is not carried beyond a limited extent, and that we then reach particles which cannot be further divided by any chemical process now known. These are the chemical atoms, and the atom is simply the unit of the chemist, just as the molecule is the unit of the physicist, or the stars are the units of the astronomer. The molecule is a group of atoms, and is a unit in the microcosm of which it is a part, in the same sense that the solar system is a unit in the great stellar universe. The molecule has been defined as the smallest particle of any substance which can exist by itself, and the atom may be now defined as *the smallest mass of an element that exists in any molecule.*

When a molecule breaks up, it is not supposed that the atoms fall apart, like grains of sand, but simply that they arrange themselves in new groups, and thus give rise to the formation

of new substances. Indeed, as a rule, the atoms cannot exist in a free state, and with few exceptions every molecule consists of at least two atoms. This is true, even of the chemical elements. The difference between the molecules of an elementary substance and those of a compound is merely this, that, while the first are formed by the union of atoms of the same kind, the last comprise atoms of different kinds. The molecules of oxygen gas are atomic aggregates as well as those of water, only the molecules of oxygen consist of oxygen atoms alone, while the molecules of water contain both oxygen and hydrogen atoms. Such at least is the constitution of most elementary substances. Nevertheless, in the case of mercury, zinc, cadmium, and some other metallic elements, the molecule consists of but one atom, or, in other words, in these cases the molecule and the atom are the same.

20. **Atomic Weights.** — There must be evidently as many kinds of atoms as there are elementary substances; and, since these substances always unite in definite proportions, it must be also true that the elementary atoms have definite weights. This once assumed, the law of multiple proportions, as well as that of definite proportions, becomes an essential part of our atomic theory; for, since the atoms are by definition indivisible, the elements can only combine atom by atom, and must therefore unite either in the proportion of the atomic weights or in some simple multiples of this proportion. We have no positive knowledge as to the absolute weights of atoms; but, after we have determined, from considerations hereafter to be discussed, what must be the number of atoms of each kind in one molecule of any substance, we can easily calculate their relative weights from the results of analysis. A few examples will make the method plain.

1st. The analysis of water, given on page 9, proves that in 100 parts it contains 11.112 parts of hydrogen and 88.888 parts of oxygen. Every molecule of water, then, must contain these two elements in just these proportions. Now we have good reason for believing that each molecule of water is a group of three atoms, — two of hydrogen and one of oxygen. Then, since

½ (11.112) : 88.888 = 1 : 16, it follows that the oxygen atom must weigh 16 times as much as the hydrogen atom; and, if we make the hydrogen atom the unit of our atomic weight, then the weight of the oxygen atom, estimated in these units, must be 16.

2d. The analysis of hydrochloric acid gas proves that it contains in 100 parts 2.74 parts of hydrogen and 97.26 of chlorine. Moreover, we have reason to believe that each molecule of the acid is a group of two atoms, — one of hydrogen and one of chlorine. Hence the atom of chlorine must weigh 35.5 times as much as that of hydrogen. Its atomic weight is then 35.5.

3d. The analysis of common salt (page 9) proves that it contains in 100 parts 60.68 parts of chlorine and 39.32 parts of sodium, and we believe that each molecule of salt is a group of two atoms, one of chlorine and one of sodium. Then, since 60.68 : 39.32 = 35.5 : 23, it follows that the atomic weight of sodium is 23. In like manner the atomic weights of all the chemical elements have been determined, and the numbers are given in Table II. These numbers are the fundamental data of chemical science, and the basis of almost all the numerical calculations which the chemist has to make. The elements of a compound body are always united either in the proportions, by weight, expressed by these numbers, or else in some simple multiples of these proportions; and whenever, by the breaking up of a complex compound, or by the mutual action of different substances on each other, the elements rearrange themselves, and new compounds are formed, the same numerical proportions are always preserved.

The atomic weights evidently rest on two distinct kinds of data: *first*, on the results of chemical analysis, which are facts of observation, and in regard to which the only question can be as to their greater or less accuracy; *secondly*, on our conclusions in regard to the number of atoms in each molecule of the substance analyzed. This conclusion again is based chiefly on two classes of facts, whose bearing on the subject we must briefly consider.

In the first place, we carefully compare together all the compounds of the element we are studying, with the view of discovering the smallest weight of it which enters into the composition of any known molecule; for this must evidently be the atomic weight of the element. An example will make the course of reasoning intelligible.

In the table on the next page we give a list of a number of the most important compounds containing hydrogen, all of which either are gases, or can easily be changed into vapor by heat, so that their specific gravities with reference to hydrogen gas can be readily determined in the aeriform state. From these specific gravities we learn the weights of the molecules (§ 18). The molecular weights, however, which are given in the third column of our table, are not in all cases exactly the values which would be obtained by doubling the gas or vapor densities referred to hydrogen gas; but they are these values corrected by the results of chemical analysis, that is, by our knowledge of the exact proportions in which the substances are known to unite or to react on each other. (Compare § 18 and your answers to problem 31 of last chapter.) In the fourth column we have given the weight of hydrogen contained in each of the molecules, weights which have in every case been calculated from the results of actual analysis; and it is obvious that, if we know the per cent of hydrogen in any substance, we can easily find the amount of this element in a single molecule of the substance when the weight of the molecule is given.

Assuming now, as in § 18, that a molecule of hydrogen gas weighs 2, it appears that the smallest mass of hydrogen which the molecule of any known substance contains, weighs just one half as much, or 1. We infer, therefore, that this mass of hydrogen cannot be divided by any chemical means, or, in other words, that it is the hydrogen atom. The molecule of hydrogen gas contains then two hydrogen atoms, and this atom is the unit to which we refer all molecular and atomic weights.

If now, in like manner, we bring into comparison all the volatile compounds of oxygen as in the second table, we shall find that the smallest mass of oxygen which exists in the molecule

ATOMIC WEIGHT OF HYDROGEN.

Compounds of Hydrogen.	Observed Sp. Gr.	Weight of Molecule.	Weight of Hydrogen in Molecule.
		m. c.	m. c.
Hydrochloric acid	18.32	36.5	1
Hydrobromic acid	39.10	81.	1
Hydriodic acid	64.12	128.	1
Hydrocyanic acid	13.67	27.	1
Water	9.00	18.	2
Hydric sulphide	17.19	34.	2
Hydric selenide	40.33	81.5	2
Ammonia gas	8.53	17.	3
Hydric phosphide	17.09	34.	3
Hydric arsenide	38.90	78.	3
Acetic acid	30.07	60.	4
Olefiant gas	14.11	28.	4
Marsh gas	8.05	16.	4
Alcohol	23.28	46.	6
Ether	37.32	74.	10
Hydrogen gas	1.00	2.	2

of any known substance weighs 16, — the atom of hydrogen weighing 1, — and hence we infer that this mass of oxygen is the oxygen atom. It appears also that a molecule of oxygen gas, like a molecule of hydrogen gas, is formed by the union of two atoms.

A similar comparison of the compounds of chlorine given in the third table shows that, while the molecules of chlorine gas weigh 71 microcriths, the atom weighs just one half as much (35.5 m. c.), so that here again the molecule consists of two atoms.

Lastly, the fourth table presents a comparison of some of the volatile compounds of carbon. This table might be very greatly extended, and with the same general results, namely, a repetition of 12 or of a multiple of 12 microcriths of carbon in every molecule of any carbon compound.

When now we remember that the numbers given in these tables are based on experimental results, it is difficult to resist the conclusion that the 12 microcriths of carbon, the 35.5

ATOMIC WEIGHT OF OXYGEN.

Compounds of Oxygen.	Observed Sp. Gr.	Weight of Molecule.	Weight of Oxygen in Molecule.
		m. c.	m. c.
Water	9.00	18.	16
Carbonic oxide	13.95	28.	16
Nitric oxide	14.97	30.	16
Alcohol	23.28	46.	16
Ether	37.32	74.	16
Carbonic dioxide	22.06	44.	32
Nitric dioxide	24.82	46.	32
Sulphurous dioxide	32.24	64.	32
Acetic acid	30.07	60.	48
Sulphuric trioxide	39.87	80.	48
Methylic borate	51.80	104.	48
Ethylic borate	74.20	146.	48
Ethylic silicate	105.60	208.	64
Osmic tetroxide	128.30	263.2	64
Oxygen gas	15.95	32.	32

microcriths of chlorine, the 16 microcriths of oxygen, and the 1 microcrith of hydrogen, which in these several classes of compounds reappear with so much constancy, are the weights of definite masses of matter. These masses are the atoms of our chemical philosophy. It will be noticed that in each case the atom is the smallest mass of an element that exists in any molecule, and hence that this method of determining its value accords completely with the definition in § 19. The same method can be extended to a large number of the chemical elements, and the conclusions to which it leads are evidently legitimate, and cannot be set aside, until it can be shown that some substance exists whose molecule contains a smaller mass of any element than that hitherto assumed as the atomic weight, or, in other words, until the old atom has been divided.

The second class of facts on which we rely for determining the number of atoms in a given molecule is based on the specific heat of the elements (compare § 17). Excepting only a few anomalies, it is certainly approximately true, and it is probably absolutely true that the specific heat of all the atoms is the same,

ATOMIC WEIGHT OF CHLORINE.

Compounds of Chlorine.	Observed Sp. Gr.	Weight of Molecule.	Weight of Chlorine in Molecule.
		m. c.	m. c.
Hydrochloric acid	18.32	36.5	35.5
Acetylic chloride	41.42	78.5	35.5
Ethylic chloride	32.02	64.5	35.5
Phosgene gas	49.06	99.	71.
Dicarbonic dichloride	.....	95.	71.
Chromic oxychloride	79.40	155.2	71.
Arsenious chloride	90.90	181.5	106.5
Boric chloride	56.85	117.5	106.5
Phosphorous chloride	68.44	137.5	106.5
Carbonic tetrachloride	78.14	154.	142.
Dicarbonic tetrachloride	84.00	166.	142.
Silicic chloride	85.72	170.	142.
Tantalic chloride	184.70	359.4	177.5
Columbic chloride	138.60	271.4	177.5
Aluminic chloride	134.80	267.8	213.
Dicarbonic hexachloride	117.70	237.	213.
Chlorine gas	35.22	71.	71.

or, in other words, that the same quantity of heat will raise the temperature of an atom of mercury or of an atom of hydrogen one degree, although the weight of the last is two hundred times greater than that of the first. If this is true, we might expect that equal amounts of heat would raise to the same extent the temperatures of such quantities of the various elementary substances as contain the same number of atoms, provided, of course, that these atomic aggregates are compared under the same conditions. Now we can determine accurately the number of units of heat required to raise the temperature of equal weights of the elementary substances one degree, and the results, which we call the specific heat of the elements, are given in works on physics (Chem. Phys. 232). Evidently, if our principle is true, these values must be proportional in every case to the number of atoms of each element contained in the equal weights compared. Representing then by S and S' the specific heat of two elementary substances, by m and m' the weights of the corresponding atoms,

ATOMIC WEIGHT OF CARBON.

Compounds of Carbon.	Observed Sp. Gr.	Weight of Molecule.	Weight of Carbon in Molecule.
		m. c.	m. c.
Marsh gas	8.05	16	12
Olefiant gas	14.11	28	24
Propylic alcohol	.....	60	36
Ether	37.32	74	48
Amylic alcohol	.....	88	60
Triethylstibine	104.40	209	72
Toluol	.....	98	84
Oil of wintergreen	.....	152	96
Cumol	.....	120	108
Oil of turpentine	.....	136	120
Amyl benzol	.....	148	132
Diphenylamine	.....	169	144

and by unity the equal weights compared, we shall have, in any case,

$$S : S' = \frac{1}{m} : \frac{1}{m'}, \text{ or } mS = m'S', \qquad [16]$$

that is, *The product of the atomic weight of an elementary substance by its specific heat is always a constant quantity.*

Taking now the atomic weights obtained by the method first given, and the specific heats of the elements as they have been determined by experimenting on these substances in the solid state, we find that, with only three exceptions, our inference is correct; and this principle not only frequently enables us to fix the atomic weight of an element, when the first method fails, but it also serves to corroborate the general accuracy of our results. It is true, owing undoubtedly to many causes which influence the thermal conditions of a solid body, that this product is not absolutely constant. It varies between 5.7 and 6.9, the mean value being about 6.34 (see Table IV.). But the variation is not important, so far as the determination of the atomic weights is concerned. This determination, as we have seen, rests chiefly on the results of analysis. The question always is only between two or three possible hypotheses, and as between these the specific heat will decide. For example, an analysis of chloride of

silver proves that each molecule contains for one atom, or 35.5 parts of chlorine, 108 parts of silver. Now, 108 parts of silver may represent one, two, three, or four atoms, or it may be that this quantity only represents a fraction of an atom. To determine, we divide 6.34 by 0.057, the specific heat of silver. The result is 111, which, though not the exact atomic weight, is near enough to show that 108 is the weight of one atom, and not of two or three. The exceptions to this rule referred to above are carbon, boron, and silicon. But it has recently been found that the specific heat of these substances varies very rapidly with the temperature, and that at a high temperature it nearly conforms to the law in each case. These results indicate that the variations are all due to differences of aggregation, and that the law would exactly hold if the atoms were isolated.

This important law, whose bearing on our subject we have briefly considered, was first discovered by Dulong and Petit, and was subsequently verified by the very careful experiments of Regnault. More recently it has been found, by Voestyn and others, that its application extends, in some cases at least, to chemical compounds; for it would seem that the atoms retain, even when in combination, their peculiar relations to heat, so that the product of the specific heat of a substance by its molecular weight is equal to as many times 6.3 as there are atoms in the molecule. Thus the specific heat of common salt, multiplied by its molecular weight, gives $0.214 \times 58.5 = 12.52$, which is very nearly equal to 6.3×2; while in the case of corrosive sublimate the corresponding product, $0.069 \times 271 = 18.70$, is nearly equal to 6.3×3, — results which are in accordance with our views in regard to the number of atoms in the molecules of these substances.

We have here, then, an obvious method by which we might determine the number of atoms in the molecule of any solid, and which would be of the very greatest value in investigating the atomic weights, could we rely on the general application of our law. We do not look for mathematical exactness. We know very well that the specific heat of solid bodies varies very greatly with the temperature, as well as from other physical causes, and

that it is impossible to compare them under *precisely the same* conditions as would be required in order to secure accordance. But, unfortunately, the discrepancies are so great, and we are so ignorant of their cause, that as yet we have not been able to use the specific heat as a means of determining the number of atoms in the molecule of a compound, except to a limited extent.

Assuming that it would require absolutely the same amount of heat to raise to a given extent the temperature of any atom, whatever its weight, when the atom is isolated, we should not expect, from our mechanical theory of heat, that this would be any longer the case when the atoms were united in a molecule; for then a portion of the heat must be spent in pulling apart the atoms, that is, in doing the work which the resulting expansion implies. If the atoms were isolated, all the heat would be expended in raising their temperature, that is, in imparting moving power. But when the atoms are bound together by definite forces, only a part of the heat is thus expended. The rest does work, and as the work done in moving apart the atoms must depend on their relations to each other, it is evident that the heat so consumed must be a very variable quantity. But although the results of investigation are in harmony with these theoretical conceptions, we have not as yet obtained the knowledge required to calculate what must be the result under given conditions. In the case of the molecules of elementary substances, where the atoms are united by comparatively feeble forces, the amount of heat expended in work is probably an inconsiderable portion of the whole; and here may be the explanation of the general conformity of the specific heat of these substances with the law just enunciated. But this cannot be true of the molecules of compound bodies, where the atoms are held together with such power that gravitation, and even molecular attraction, are feeble forces in comparison. Hence the difficulty of bringing the specific heat of compounds under the general law; but we have every reason to expect that in proportion as our knowledge of molecular structure increases this result will be reached. It must be borne in mind, however, that the problem is still further complicated by

the fact that, when a body is expanded by heat, work is done in moving apart the molecules as a whole, as well as the atoms of which the molecules consist.

Lastly, assuming that both of the means we have considered fail to give satisfactory evidence in regard to the number of atoms in the molecule of a given substance, (which we may have analyzed for the purpose of determining some atomic weight,) we may frequently, nevertheless, reach a satisfactory, or at least a probable conclusion, by comparing the substance we are investigating with some closely allied substance whose constitution is known. Thus, if the molecule of sodic chloride (common salt) contains two atoms, it is probable that the molecules of sodic iodide, as well as those of potassic chloride and potassic iodide, contain the same number; for all these compounds not only have the same crystalline form and the same chemical relations, but they are also composed of closely allied chemical elements. Nevertheless it is true, in very many cases, that our conclusion in regard to the number of atoms which a molecule may contain is more or less hypothetical, and hence liable to error and subject to change. This uncertainty, moreover, must extend to the atomic weights of the elements, so far as they rest on such hypothetical conclusions.

If we change the hypothesis in any case, we shall obtain a different atomic weight; but then the new weight will be some simple multiple of the old, and will not alter the important relations to which we first referred. These fundamental relations are independent of all hypothesis, and rest on well-established laws.

The atomic weights are the numerical constants of chemistry, and in determining their value it is necessary to take that care which their importance demands. The essential part of the investigation is the accurate analysis of some compound of the element whose atomic weight is sought. The compound selected for the purpose must fulfil several conditions. It must be one which can be prepared in a condition of absolute purity. It must be one the proportions of whose constituents can be determined with the greatest accuracy by the known methods of

analytical chemistry. It must contain a second element whose atomic weight is well established. Finally, it should be a compound whose molecular condition is known, and it is best that this should be as simple as possible. When once thus accurately determined, the atomic weights become essential data in all quantitative analytical investigations.

QUESTIONS AND PROBLEMS.

1. Does the integrity of a substance reside in its molecules or in its atoms?

2. We find by analysis that in 100 parts of potassic chloride there are 52.42 parts of potassium and 47.58 parts of chlorine. Moreover, we know from previous experiments that the atomic weight of chlorine is 35.5, and we have reason to believe that every molecule of the compound consists of 2 atoms, 1 of potassium and 1 of chlorine. What is the atomic weight of potassium? Ans. 39.1.

3. We find by analysis that in 100 parts of phosphoric anhydride there are 43.66 parts of phosphorus and 56.34 parts of oxygen. Moreover, we know that the atomic weight of oxygen is 16; and we have reason to believe that every molecule of the compound consists of 7 atoms, 2 of phosphorus and 5 of oxygen. What is the atomic weight of phosphorus? Ans. 31.

4. In Table III. the student will find the vapor densities of a number of compounds of arsenic, and we give below the per cent of arsenic which each contains. From these data it is required to determine the atomic weight of arsenic. Arrange the results in a table like those given above. Metallic arsenic, 100 per cent; arseniuretted hydrogen, 96.16 per cent; arsenious chloride, 41.32 per cent; kakodyl, 71.44 per cent; arsenious oxide, 75.77 per cent.

5. Review the steps of the reasoning by which the atomic weights have been deduced in the last two problems, and show that the *molecular weight* and *the weight of the element in one molecule* are actual and independent experimental data.

6. Analysis shows that in 100 parts of mercuric chloride there are 73.80 parts of mercury and 26.20 parts of chlorine. The specific

heat of mercury is 0.032. What is the probable atomic weight of mercury, that of chlorine being 35.5? Also, how many atoms of each element does one molecule of the compound contain?

Ans. Atomic weight of mercury, 200. Each molecule consists of 1 atom of mercury and 2 of chlorine.

7. Analysis shows that in 100 parts of ferric oxide there are 70 parts of iron and 30 parts of oxygen. The specific heat of iron is 0.114. What is the probable atomic weight of iron, that of oxygen being 16? and how many atoms of each element does one molecule of the oxide contain?

Ans. Atomic weight of iron, 56. One molecule of ferric oxide contains 2 atoms of iron and 3 of oxygen.

8. There is no doubt that in oxide of glucinum the metal is combined with oxygen in the proportion of 9.2 to 16, and it has been hitherto generally assumed that each molecule of the oxide consists of one atom of glucinum united to one of oxygen, and hence that the atomic weight of this rare element is 9.2. But it appears from recent experiments that the specific heat of glucinum is 0.408. To what conclusion does this new fact lead?

Ans. That the atomic weight of glucinum is 13.8, and that each molecule of its oxide consists of 2 atoms of metal and 3 atoms of oxygen.

9. The molecular weight of silicic chloride is 170, and its specific heat, 0.1907. How many atoms does one molecule of the compound probably contain? Ans. 5.

10. The molecular weight of mercuric iodide is 454, and its specific heat, 0.042. How many atoms does one molecule of the compound probably contain? Ans. 3.

CHAPTER V.

CHEMICAL NOTATION.

21. **Chemical Symbols.** — The atomic theory has found expression in chemistry in a remarkable system of notation, which has been of the greatest value in the study of the science. In this system, the initial letter of the Latin name of an element is used as the symbol of that element, and represents in every case *one atom*. Thus *O* stands for *one atom* of Oxygen, *N* for *one atom* of Nitrogen, *H* for *one atom* of Hydrogen. When several names have the same initial, we add for the sake of distinction a second letter. Thus *C* stands for one atom of Carbon, *Cl* for one atom of Chlorine, *Ca* for one atom of Calcium, *Cu* for one atom of Cuprum (copper), *Cr* for one atom of Chromium, *Co* for one atom of Cobalt, *Cd* for one atom of Cadmium, *Cs* for one atom of Cæsium, and *Ce* for one atom of Cerium. The symbols of all the elements are given in Table II. Several atoms of the same element are generally indicated by adding figures, but distinguishing them from algebraic exponents by placing them below the letters. Thus Sn_2 stands for two atoms of Stannum (tin), S_3 for three atoms of Sulphur, and I_5 for five atoms of Iodine. Sometimes, however, in order to indicate certain relations, we repeat the symbol with or without dashes between them; thus *H-H* represents a group of two atoms of Hydrogen, *Se=Se* a group of two atoms of Selenium. We can now easily express the constitution of the molecule of any substance by simply grouping together the symbols of the atoms of which the molecule consists. This group is generally called the symbol of the substance, and stands in every case for one molecule. Thus *NaCl* is the symbol of common salt, and represents one molecule of salt. H_2O is the symbol of water, and represents, as before, one molecule. So in like manner H_3N stands for one

molecule of ammonia gas, H_4C for one molecule of marsh gas, KNO_3 for one molecule of saltpetre, H_2SO_4 for one molecule of sulphuric acid, $C_2H_4O_2$ for one molecule of acetic acid, $H\text{-}H$ for one molecule of hydrogen gas. We do not, however, always write the symbols in a linear form, but group the letters in such a way as will best indicate the relations we are studying. When several molecules of the same substance take part in a chemical change, we represent the fact by writing a numerical coefficient before the molecular symbol. A figure so placed always multiplies the whole symbol. Thus $4\,H\text{-}NO_3$ stands for four molecules of nitric acid, $3\,C_2H_6O$ for three molecules of alcohol, $6\ O\text{-}O$ for six molecules of oxygen gas. When clearness requires it, we enclose the symbol of the molecule in parentheses, thus, $4(H_3{=}N)$, or $(H_3{=}N)_4$. The precise meaning of the dashes will hereafter appear. They are used, like punctuation marks, to point off in a molecular symbol the parts between which we wish to distinguish.

22. **Chemical Reactions.** — These chemical symbols give at once a simple means of representing all chemical changes. As these changes almost invariably result from the *reaction* of one substance on another, they are called *chemical reactions*. Such reactions must necessarily take place between molecules, and simply consist in the breaking up of the molecules and the rearrangement of the atoms in new groups. In every chemical reaction we must distinguish between the substances which are involved in the change and those which are produced by it. The first will be termed the factors, and the last the products, of the reaction. As matter is indestructible, it follows that *the sum of the weights of the products of any reaction must always be equal to the sum of the weights of the factors*, and, further, that *the number of atoms of each element in the products must be the same as the number of atoms of the same kind in the factors*. This statement seems at first sight to be contradicted by experience, since wood and many other combustibles are consumed by burning. In all such cases, however, the apparent annihilation of the substance arises from the fact that the products of the change are invisible gases; and when these are collected,

their weight is found to be equal, not only to that of the substance, but also, in addition, to the weight of the oxygen from the air consumed in the process. As the products and factors of every chemical change must be equal, it follows that *a chemical reaction may always be represented in an equation by writing the symbols of the factors in the first member, and those of the products in the second.* Thus, the following equation expresses the reaction between dilute sulphuric acid and zinc, by which hydrogen gas is commonly prepared. The products are a solution of zinc sulphate and hydrogen gas.

$$\mathbf{Zn} + (H_2SO_4 + Aq) = (ZnSO_4 + Aq) + \mathbb{H}\text{-}\mathbb{H}. \qquad [17]$$

The abbreviation of the Latin word *Aqua* is here used simply to indicate that the substances enclosed with it in parentheses are in solution. The symbol **Zn** is printed in "full-faced" type to indicate that the metal is used in the reaction in its well-known solid condition; while the symbol of the molecule of hydrogen is printed in skeleton type to indicate the condition of gas. This usage will be followed throughout the book; but, generally, when it is not important to indicate the condition of the materials involved in the reaction, ordinary type will be used. The molecule of hydrogen gas consists of two atoms, as our reaction indicates, and this is the smallest quantity of hydrogen which can either enter into or be formed by a chemical change. The molecule of zinc is known to consist of only one atom. When the molecular constitution of an element is not known, we simply write the atomic symbol in the reaction.

Among chemical reactions we may distinguish at least three classes. First, Analytical Reactions, in which a complex molecule is broken up into simpler ones. Thus, when sodic bisulphate is heated, it breaks up into sodic sulphate and sulphuric anhydride, —

$$Na_2S_2O_7 = Na_2SO_4 + SO_3. \qquad [18]$$

So, also, by fermentation grape sugar or glucose breaks up into alcohol and carbonic anhydride, —

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2. \qquad [19]$$

Secondly, Synthetical Reactions, in which two molecules unite to form a more complex group. Thus baryta burns in an atmosphere of sulphuric anhydride, and forms baric sulphate, —

$$BaO + SO_3 = BaSO_4. \qquad [20]$$

In like manner ammonia enters into direct union with hydrochloric acid to form ammonic chloride, —

$$H_3N + HCl = H_4NCl. \qquad [21]$$

Thirdly, Metathetical Reactions, in which the atoms of one molecule change place with the similar atoms of another molecule or of several other molecules, one atom replacing one, two, three, or more atoms, as the case may be. Thus, when we add a solution of common salt to a solution of argentic nitrate, we obtain a white precipitate * of argentic chloride, while sodic nitrate remains in solution. The result is obtained by a simple interchange between an atom of silver and an atom of sodium, as the following reaction shows: —

$$(Na\text{-}Cl + Ag\text{-}NO_3 + Aq) = (Na\text{-}NO_3 + Aq) + \mathbf{Ag\text{-}Cl}. \qquad [22]$$

In the next example, one atom of barium changes place with two atoms of hydrogen. Baric chloride and sulphuric acid yield hydrochloric acid and insoluble baric sulphate, which is precipitated from the solution in water as the reaction indicates: —

$$(BaCl_2 + H_2SO_4 + Aq) = (2\,HCl + Aq) + \mathbf{BaSO_4}. \qquad [23]$$

Of the three classes of chemical reactions the last is by far the most common, and many chemical changes which were formerly supposed to be examples of simple analysis or synthesis are now known to be the results of metathesis. In very many cases, however, a chemical reaction cannot be explained in either of these ways alone, but seems to consist in a primary union of two or more molecules and a subsequent splitting up of this large group. Indeed, this is the best way of conceiving of all

* The separation of a solid or sometimes of a liquid substance in a fluid menstruum, as the result of a chemical reaction, is called precipitation, and the material which separates, a precipitate; and this, too, even when the material, being lighter than the fluid, rises instead of falls.

metathetical reactions, for we do not suppose that in any case there is an actual transfer of atoms from one molecule to the other. The word *metathesis* is merely used to indicate the result of the process, not the manner in which the change takes place, and the same is true of the words *analysis* and *synthesis*. The common method of preparing carbonic anhydride is to pour a solution of hydrochloric acid on small lumps of marble (calcic carbonate), —

$$\mathrm{CaCO_3} + (2\,HCl + Aq) = (CaCO_3\,H_2Cl_2 + Aq) \qquad [24]$$
$$= (CaCl_2 + H_2O + Aq) + \mathrm{CO_2}.$$

We may suppose that the molecules of the two substances are, in the first place, drawn together by the force which manifests itself in the phenomena of adhesion,* but that, as they approach, a mutual attraction between their respective atoms comes into play, which, the moment the molecules come into collision, causes the atoms to arrange themselves in new groups. The groups which then result are determined by many causes whose action can seldom be fully traced; but there are two conditions which, in the presence of a liquid medium, have a very important influence on the result. These conditions may be thus stated: —

1st. Whenever a compound can be formed, which is insoluble in the menstruum present, this compound separates as a precipitate.

2d. Whenever a gas can be formed, or any substance which is volatile at the temperature at which the experiment is made, this volatile product is set free.

The reactions [22] and [23] of this section are examples of the first, while the reactions [17] and [24] are examples of the second of these conditions. The facts just stated illustrate an important truth, which must be carefully borne in mind in the study of chemistry. A chemical equation differs essentially from an algebraic expression. Any inference which can be legitimately

* We find it convenient to distinguish between the force which holds together different molecules and that which unites the atoms of the molecules. To the last we give the name of *chemical affinity*, while we call the first *cohesion* or *adhesion*, according as it is exerted between molecules of the same kind or those of a different kind.

drawn from an algebraic equation must, in some sense, be true. It is not so, however, with chemical symbols. These are simply expressions of observed facts, and, although important inferences may sometimes be drawn from the mere form of the expression, yet they are of no value whatever unless confirmed by experiment. Moreover, the facts which are expressed in this peculiar system of notation are as purely materials for the memory as if they were described in common language.

23. **Compound Radicals.** — In many chemical reactions the elementary atoms change places, not with other elementary atoms, but with groups of atoms, which appear to sustain relations to the compounds they leave or enter, similar to those of the elements themselves. Thus, if we add to a solution of argentic nitrate a solution of ammonic chloride, we get the reaction expressed by the equation

$$Ag\text{-}NO_3 + NH_4\text{-}Cl = NH_4\text{-}NO_3 + Ag\text{-}Cl. \qquad [25]$$

Here the group NH_4 has taken the place of Ag. So, also, in the reaction of hydrochloric acid on common alcohol, the group C_2H_5 in the molecule of alcohol changes places with the atom of hydrogen in the molecule of hydrochloric acid, —

$$\underset{\text{Alcohol.}}{C_2H_5\text{-}OH} + H\text{-}Cl = H\text{-}OH + \underset{\text{Ethylic Chloride.}}{C_2H_5\text{-}Cl}. \qquad [26]$$

We write the symbols in this peculiar way in order to make it evident to the eye that such a substitution has taken place. Lastly, in the reaction of chloroform on ammonia, the group CH of the first changes places with the three atoms of hydrogen of ammonia gas, —

$$\underset{\text{Chloroform.}}{CH\text{-}Cl_3} + H_3\text{-}N = 3\,HCl + \underset{\text{Hydrocyanic Acid.}}{CH\text{-}N}. \qquad [27]$$

Such groups as these are called compound radicals. Like the atoms themselves, they cannot, as a rule, exist in a free state; but aggregates of some of these radicals may exist, which sustain the same relation to the radicals that elementary substances hold to the atoms. Thus, as we have a gas chlorine consisting of molecules, each represented by $Cl\text{-}Cl$, so there is a gas cyanogen consisting of molecules, each represented by $CN\text{-}CN$, where CN is a

compound radical called cyanogen. Again, the important radicals CO, SO_2, and PCl_3 are also the molecules of well-known gases. These *radical substances* correspond to certain elementary substances previously mentioned, in which the molecule is a single atom.

But with few exceptions the radical substances have never been isolated, and the radicals are only known as groups of atoms which pass and repass in a number of chemical reactions. Indeed, in the same compound we may frequently assume several radicals. The possible radicals of a chemical symbol correspond in fact almost precisely to the possible factors of an algebraic formula, and in writing the symbol we take out the one or the other, as the chemical change we are studying requires. A number of these radicals have received names; as, —

Hydroxyl,	HO	Sulphuryl,	SO_2
Hydrosulphuryl,	HS	Carbonyl,	CO
Ammonium,	H_4N	Carboxyl,	$COOH$
Amidogen,	H_2N	Nitrosyl,	NO
Cyanogen,	CN	Nitroxyl,	NO_2.

But the names are not of importance, and the usage in regard to them has never been fixed.

QUESTIONS AND PROBLEMS.

1. For what do the following symbols stand?

$$N;\ Ca_2;\ H\text{-}H;\ H_4C;\ 4\,HNO_3;\ (C_2H_4O_2)_3.$$

2. For what do the following symbols stand?

$$Cl;\ S_3;\ O{=}O;\ H_3N;\ H_2SO_4;\ 3\,C_2H_6O.$$

3. For what do the following symbols stand?

$$O;\ H_5;\ Se{=}Se;\ NaCl;\ H_2O;\ 3\,KNO_3.$$

4. Represent by symbols, — 1st, 5 molecules of water; 2d, 3 molecules of calcic carbonate; 3d, 2 molecules of baric sulphate; 4th, 1 molecule of sodic disulphate.

5. Analyze the following reaction. Show that the same number of atoms are represented on each side of the equation, and state the class to which it belongs.

$$\underset{}{Fe} + \underset{\text{Hydrochloric Acid.}}{(2\,HCl + Aq)} = \underset{\text{Ferrous Chloride.}}{(FeCl_2 + Aq)} + \underset{}{H\text{-}H}.$$

6. Analyze the following reaction. Show in what the equality consists, and state the class to which the reaction belongs.

$$\underset{\text{Ammonic Nitrate.}}{N_2H_4O_3} = \underset{\text{Water.}}{2\,H_2O} + \underset{\text{Nitrous Oxide.}}{N_2O}.$$

7. Analyze the following reactions. Show in what the equality consists, and state the class to which the reaction belongs.

$$\underset{\text{Carbon.}}{C} + \underset{\text{Oxygen.}}{O\text{-}O} = \underset{\text{Carbonic Dioxide.}}{CO_2}.$$

8. Analyze the following reaction. Show in what the equality consists, and state the class to which the reaction belongs.

$$\underset{\text{Water.}}{2\,H\text{-}O\text{-}H} + \underset{\text{Sodium.}}{Na\text{-}Na} = \underset{\text{Sodic Hydrate.}}{2\,Na\text{-}O\text{-}H} + H\text{-}H.$$

9. The following reaction may be so written as to indicate that the products are formed by a metathesis between two similar molecules. It is required to show that this is possible.

$$\underset{\text{Ammonia Gas.}}{2\,H_3N} = \underset{\text{Hydrogen Gas.}}{3\,H\text{-}H} + \underset{\text{Nitrogen Gas.}}{N\text{-}N}.$$

10. Write the reactions [22] and [23] so as to indicate the manner in which the metathesis is supposed to take place.

11. State the conditions which determine the metathesis in the various reactions given in this chapter so far as these conditions are indicated.

12. Analyze the following reaction. Show what determines the metathesis, and also what is meant by a compound radical.

$$\underset{\text{Plumbic Nitrate.}}{(Pb(NO_3)_2} + \underset{\text{Ammonic Chloride.}}{2\,NH_4\text{-}Cl} + Aq) = \underset{\text{Plumbic Chloride.}}{PbCl_2} + \underset{\text{Ammonic Nitrate.}}{(2\,NH_4\text{-}NO_3} + Aq).$$

13. Compare with [27] the following reaction, and point out the two radicals, which, as we may assume, hydrocyanic acid contains.

$$\underset{\text{Argentic Nitrate.}}{(Ag\text{-}NO_3} + \underset{\text{Hydrocyanic Acid.}}{H\text{-}CN} + Aq) = \underset{\text{Argentic Cyanide.}}{Ag\text{-}CN} + \underset{\text{Nitric Acid.}}{(H\text{-}NO_3} + Aq).$$

14. When sulphuric anhydride (SO_3) is added to water (H_2O) a violent action ensues and sulphuric acid is formed. The reaction may be written in two ways, and it is required to explain the different views of the process, which the following equations express.

$$H_2O + SO_3 = H_2SO_4;$$

or,

$$2\,H\text{-}O\text{-}H + SO_2{=}O = H_2{=}O_2{=}SO_2 + H_2{=}O.$$

15. State the distinction between a chemical element and an elementary substance. Give also the distinction between a compound radical and a radical substance.

CHAPTER VI.

STOCHIOMETRY.

24. **Stoichiometry.**—The chemical symbols enable us not only to represent chemical changes, but also to calculate exactly the amounts of the substances required in any given process, as well as the amounts of the products which it will yield. Each symbol stands for a definite weight of the element it represents, that is, for the weight of an atom; but, as only the relative values of these weights are accurately known, they are best expressed as so many parts. Thus H, which indicates one atom of hydrogen, stands for 1 part by weight of hydrogen, the unit of our system. In like manner O stands for one atom or 16 parts by weight of oxygen, N for one atom or 14 parts by weight of nitrogen, C for one atom or 12 parts by weight of carbon, C_5 for five atoms or 60 parts by weight of carbon, and so on for all the symbols in Table II. The weight of the molecule of any substance must evidently be the sum of the weights of its atoms, and is easily found, when the symbol is given, by simply adding together the weights which the atomic symbols represent. Thus H_2O, the symbol of one molecule of water, stands also for $2 + 16 = 18$ parts of water, H_3N for one molecule, or $3 + 14 = 17$ parts of ammonia gas, and $C_2H_4O_2$ for $24 + 4 + 32 = 60$ parts of acetic acid.*

Having then given the symbol of a substance, it is very easy to calculate its percentage composition. Thus, as in 60 parts of acetic acid there are 24 parts of carbon, in 100 parts of the acid there must be 40 parts of carbon, and so for each of the other elements. The result appears below; and in the same

* In this book *the molecular weight of a substance* will always mean the sum of the atomic weights of the atoms composing *one* molecule, and we shall employ *the molecular weight of a symbol*, or *the total atomic weight* which it represents, to denote the sum of the atomic weights of all the molecules which that symbol represents.

way the percentage composition of alcohol and ether has been calculated from the accompanying symbols.

	Acetic Acid, $C_2H_4O_2$.	Alcohol, C_2H_6O.	Ether, $C_4H_{10}O$.
Carbon,	40.00	52.18	64.86
Hydrogen,	6.67	13.04	13.52
Oxygen,	53.33	34.78	21.62
	100.00	100.00	100.00

The rule, easily deduced, is this: *As the weight of the molecule is to the weight of each element, so is one hundred parts to the percentage required.*

On the other hand, having given the percentage composition, it is easy to calculate the number of atoms of each element in the molecule of the substance. This problem is evidently the reverse of the last, but it does not, like that, always admit of a definite solution; for, while there is but one percentage composition corresponding to a given symbol, there may be an infinite number of symbols corresponding to a given percentage composition. For example, the percentage composition of acetic acid corresponds not only to the formula $C_2H_4O_2$, given above, but also to any multiple of that formula, as can easily be seen by calculating the percentage composition of CH_2O, $C_3H_6O_3$, $C_4H_8O_4$, etc. They will all necessarily give the same result, and, before we can determine the absolute number of atoms of each element present, we must have given another condition; namely, the sum of the weights of the atoms, or, in other words, the molecular weight of the substance. When this is known, the problem can at once be definitely solved.

Suppose we have given the percentage composition of alcohol, as above, and also the further fact that its molecular weight is 46. We can then at once make the proportions

$100 : 52.18 = 46 : x = 24$, the weight of the atoms of carbon;
$100 : 13.04 = 46 : x = 6$, " " " hydrogen;
$100 : 34.78 = 46 : x = 16$, " " " oxygen.

Then it follows that

$\frac{24}{12} = 2$, the number of atoms of carbon in one molecule;
$\frac{6}{1} = 6$, " " " hydrogen in one molecule;
$\frac{16}{16} = 1$, " " " oxygen in one molecule.

It is evident from this example, that, in order to determine exactly the symbol of a compound, we must know at least its *approximate* molecular weight. Evidently it is not essential that we should know the *exact* molecular weight, but only that we should know the value with sufficient accuracy to enable us to select between a few possible multiples. Thus, in the case of alcohol, the molecular weight must be either 23, or a multiple of 23, and a very rough approximation to its value will enable us to decide this question. When the substance is a gas, or is capable of being changed into vapor, *without decomposition*, we can easily determine its approximate molecular weight by the principle of § 18, that is, by doubling its specific gravity referred to hydrogen; and for all the problems given in this book which deal only with the common gases and vapors, the molecular weight can be at once taken from Table III. If we are dealing with a new substance, we must determine its specific gravity experimentally by one of the methods already described.

When, on account of the fixed nature of the substance, the last mode of investigation is impossible, we can still frequently draw trustworthy conclusions in regard to its molecular weight after studying the chemical reactions into which the substance enters, and thus comparing it with substances whose molecular weights are known. The methods used in such cases will be described hereafter, and then the validity of the conclusion can be better appreciated; but even when all such means fail, we can nevertheless always find which of all possible symbols expresses the composition of the substance we are studying in the simplest terms, in other words, with the fewest number of atoms in the molecule. Suppose the substance to be cane sugar, which cannot be volatilized without decomposition, and of which no reaction is known which gives any definite clew to its molecular weight. Péligot's analysis, cited on page 9, shows that it contains, in 100 parts, 42.06 parts of carbon, 6.50 parts of

hydrogen, and 51.44 parts of oxygen. Assume for the moment that the molecular weight is equal to 100, then

$$\frac{42.06}{12} = 3.50, \text{ the number of atoms of carbon;}$$

$$\frac{6.50}{1} = 6.50, \quad " \quad " \quad " \quad \text{hydrogen;}$$

$$\frac{51.44}{16} = 3.22, \quad " \quad " \quad " \quad \text{oxygen.}$$

This would be the number of atoms of each element if the sum of the atomic weight — that is, the molecular weight — of sugar were equal to 100. As, from the very definition, fractional atoms cannot exist, these numbers are impossible, but any other possible number of atoms must be either a multiple or a submultiple of the numbers found; and we can easily discover the fewest number of whole atoms possible, by seeking for the three smallest whole numbers which stand to each other in the relation of 3.50 : 6.50 : 3.22, a proportion which is very nearly satisfied by 12 : 22 : 11. Hence, the simplest possible symbol is $C_{12}H_{22}O_{11}$, and this has been adopted by chemists as the symbol of cane sugar, although, from anything we as yet know, the symbol may be a multiple of this. If now, taking this symbol as our starting-point, we calculate the percentage composition which would exactly correspond to it, we obtain the following results, which we have arranged in a tabular form, so that the student may compare the theoretical composition with the numbers Péligot obtained by actual analysis.

Composition of Cane Sugar,

$C_{12}H_{22}O_{11}$.

	Theoretical.	Péligot's Analysis.
Carbon,	42.11	42.06
Hydrogen,	6.43	6.50
Oxygen,	51.46	51.44
	100.00	100.00

The difference between the two is now seen to be within the probable errors of analysis, and this example illustrates the method of arranging analytical results generally adopted by chemists.

From the above discussion we can easily deduce a simple arithmetical rule for finding the symbol of a compound when its percentage composition is known. But this rule may be best expressed in an algebraic formula, which will show to the eye at once the relation of the quantities involved in the calculation, and enable us to extend our method to the solution of many classes of problems which we might not otherwise foresee. Let us then represent

By M the weight of any chemical compound in grammes.
" m the molecular weight of the compound in microcriths.
" W the weight of any constituent of that compound, whether element or compound radical, in grammes.
" w the total atomic weight of element or radical in one molecule.

Then

$\frac{w}{m}$ = proportion by weight of the constituent in the compound,

and

$M\frac{w}{m}$ = weight of constituent in M grammes of compound, or

$$W = M\frac{w}{m}. \qquad [28]$$

Any three of these quantities being given, the fourth can, of course, be found. Thus we may solve four classes of problems:—

1st. We may find the weight of any constituent in a given weight of a compound, when we know the molecular weight of the compound and the total atomic weight of the constituent in one molecule.

Problem. It is required to find the weight of sulphuric anhydride, SO_3, in 4 grammes of plumbic sulphate, PbO, SO_3. Here, $w = 32 + 3 \times 16 = 80$, $m = 207 + 16 + 80 = 303$, and $M = 4$.

Ans. 1.056 grammes.

2d. We can find the weight of a compound which can be produced from, or corresponds to, a given weight of one of its constituents, when the same quantities are known as above.

Problem. How many grammes of common crystallized green vitriol, $FeSO_4 . 7\ H_2O$, can be made from 5 grammes of iron? Here, $w = 56$, $m = 278$, $W = 5$. Ans. 24.821 grammes.

3d. We can find the molecular weight of a compound when we have given the weight of one constituent in a given weight of the compound, and the total atomic weight of that constituent in the molecule.

Problem. In 7.5 grammes of ethylic iodide, there are 6.106 grammes of iodine; the total atomic weight of iodine in one molecule is 127. What is the molecular weight of ethylic iodide? Ans. 156.

4th. We can find the total atomic weight of one constituent of a molecule when the molecular weight is given, and also the weight of the constituent in a known weight of the compound.

Problem. The molecular weight of acetic acid is 60; the per cent of carbon in the compound, 40. What is the total atomic weight of carbon in one molecule? Ans. 24.

Whence number of carbon atoms in one molecule, 2.

The last problem is essentially the same as that of finding the symbol of a compound when its percentage composition is given, while the first corresponds to the reverse problem of deducing the percentage composition from the symbol. By a slight change the formula can be much better adapted to this class of cases. For this purpose we may put $M = 100$, since we are solely dealing with per cents, and also put $w = na$, where a stands for the atomic weight of any element, and n for the number of atoms of that element in one molecule of the compound we are studying. We then have

$$W = 100\,\frac{na}{m} \text{ and } n = \frac{W}{100}\,\frac{m}{a}. \qquad [29]$$

The first of these forms is adapted for calculating the per cent of each element of a compound when the molecular weight, the number of atoms of each element in one molecule, and the several atomic weights, are known; and it is evident that all these data are given by the chemical symbol of the compound. The second of these forms enables us to calculate the number of atoms of each element present in one molecule of a compound when the percentage composition, the molecular weight, and the several atomic weights, are known, and illustrates the principle before developed, that the molecular weight is an essential element of the problem.

25. **Stochiometrical Problems.** — The principles of the previous section apply not only to single molecular formulæ, but obviously may also be extended to the equations which represent chemical changes. Since the molecular symbols which are equated in these expressions represent known relative weights,

it must be true in every case that we can calculate the weight of either of the factors or products of the chemical change represented, provided only that the weight of some one is known. If we represent by w and m the total atomic weight of any two symbols entering into the chemical equations, and by W and M the weight in grammes of the factors or products which these symbols represent, then the simple algebraic formulæ of the last section will apply to all stochiometrical problems of this kind, as well as to those before indicated. These formulæ, however, are merely the algebraic expression of the familiar rule of three, and all stochiometrical problems are solved more easily by this simple arithmetical rule. Using the word *symbol* to express the sum of the atomic weights it represents, we may state the rule as applied to chemical problems in the following words:—

Express the reaction in the form of an equation; make then the proportion, As the symbol of the substance given is to the symbol of the substance required, so is the weight of the substance given to the weight of the substance required; reduce the symbols to numbers, and calculate the value of the unknown quantity, represented, as usual, by x.

This rule applies equally well to all problems, like those of the last section, in which the elements or radicals of the same molecular symbol are alone involved; only in such cases there is of course no equation to be written. A few examples will illustrate the application of the rule.

Problem 1. We have given 10 kilogrammes of common salt, and it is required to calculate how much hydrochloric acid gas can be obtained from it by treating with sulphuric acid. The reaction is expressed by the equation

$$(2\,NaCl + H_2SO_4 + Aq) = (Na_2SO_4 + Aq) + 2\,HCl.$$

If now we find the total molecular weights of each substance by adding together the atomic weights which the symbols represent, as already fully explained, we deduce the following proportion,

$$2\,\overset{117}{NaCl} : 2\,\overset{73}{HCl} = 10 : x = \text{Ans. } 6.239 \text{ kilogrammes};$$

which simply states that as 117 parts of sodic chloride yield 73 parts of hydrochloric acid gas, so 10 kilogrammes of the salt will yield 6.239 kilogrammes of the acid.

Problem 2. It is required to calculate how much sulphuric acid and nitre must be used to make 250 grammes of the strongest nitric acid. The reaction is expressed by the equation

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3,$$

whence we get the proportions

$$\overset{63}{HNO_3} : \overset{98}{H_2SO_4} = 250 : x = 388.9 \text{ grammes sulphuric acid, 1st Ans.}$$

$$\overset{63}{HNO_3} : \overset{101.1}{KNO_3} = 250 : x = 401.2 \text{ grammes nitre, 2d Ans.}$$

The student should also solve by the same rule the problems given in the foregoing section.

26. **Gay-Lussac's Law.** — This eminent French chemist was the first to state clearly the important truth, that, when gases or vapors react on each other, the volumes both of the factors and of the products of the reaction always bear to each other some very simple numerical ratio. This truth is generally known as the law of Gay-Lussac, but, since the principle is a direct consequence of the molecular theory, it is best studied in that relation. It is, as we have seen, a fundamental postulate of the theory that equal volumes of all substances, when in the aeriform condition, contain the same number of molecules. Hence it follows, that the volumes of all single molecules are the same, and, if we take this common volume as our unit of measure, it follows, further, that the total molecular volume represented by any symbol is always equal to the number of molecules. We are thus led to a most important fact, which gives an additional meaning to our chemical symbols, for it appears that *every chemical equation, when properly written, represents not only the relative weights, but also the relative volumes of its factors and products, when in the state of gas.*

This principle is illustrated by the following equations: —

$$\boxed{CH_4} + 2\boxed{O{=}O} = \boxed{CO_2} + 2\boxed{H_2O}$$

Marsh Gas. Oxygen Gas. Carbonic Anhydride. Aqueous Vapor.

$$2\boxed{NO} + 5\boxed{H{\cdot}H} = 2\boxed{NH_3} + 2\boxed{H_2O}$$

Nitric Oxide Gas. Hydrogen Gas. Ammonia Gas. Aqueous Vapor.

The squares, which here serve to indicate equal volumes, and to impress on the mind this additional meaning which we shall now attach to our molecular symbols, are evidently unnecessary, and will not be used hereafter.

The important rule of the last section may be expressed by the following proportion: —

$$n\,m : n'm' = W : W' = \mathrm{W} : \mathrm{W}'.$$

Here m and m' represent the molecular weights of any two substances, n and n' the number of molecules of these substances which take part in a chemical reaction, whether as factors or products, while $n\,m$ and $n'm'$ represent what in the statement of our rule we have called *the symbols of the substances*, and the equation expresses the fact that the sum of the atomic weights indicated by the symbols is proportional to the weights of the substances involved in the chemical reaction, whether these weights are estimated in grammes or in criths (§ 2).

Now by (§ 18), $m' = 2$ Sp. Gr., and by [3], $\mathrm{W}' = \mathrm{V} \times$ Sp. Gr. Making these substitutions, we may reduce the above proportion to the following form: —

$$\tfrac{1}{2}\,n\,m : n' = \mathrm{W} : \mathrm{V},$$

and this gives us another stochiometrical rule by which we can calculate the *volume* of a gas or vapor involved in a chemical reaction, when the *weight* of some other factor or product is known, or, inversely, when the volume is given, calculate the weight.

Express the reaction in an equation; make then the proportion, As one half of the symbol of the first substance is to the number of molecules of the second, so is the weight in criths of the first to the volume in litres of the second; reduce the symbol to numbers, and calculate the value of the unknown quantity.

This rule has the same general application as the first, and a few examples will illustrate the use of it.

Problem 1. How much chlorate of potash must be used to obtain one litre of oxygen gas? The reaction is expressed by the equation

$$2\,KClO_3 = 2\,KCl + 3\,O{=}O,$$

whence we get the proportion

$$\tfrac{1}{2}\,(2\,\overset{122.6}{KClO_3}) : 3 = x : 1. \qquad x = 40.9 \text{ criths.}$$

$$40.9 \times 0.0896 = \text{Ans. } 3.664 \text{ grammes.}$$

Problem 2. How many litres of oxygen gas can be obtained from 500 grammes of chlorate of potash? The reaction is the same as before, but in this case the grammes must first be reduced to criths. The proportion will then be written

$$\overset{122.6}{KClO_3} : 3 = \frac{500}{0.0896} : x = \text{Ans. } 136.6 \text{ litres.}$$

Problem 3. How many litres of ammonia gas NH_3 are contained in 20 grammes of ammonic chloride, $NH_3{\cdot}HCl$? Here we require no equation; for the symbol itself gives at once the proportion

$$\tfrac{1}{2}\,NH_4Cl : 1 = \frac{20}{0.0896} : x = \text{Ans. } 8.343 \text{ litres.}$$

In applying the rules of this chapter to the solving of stochiometrical problems, the student should carefully bear in mind, *first*, that the rule of § 25 applies to all those cases in which the *weight* of one substance is to be calculated from the *weight* of another; *secondly*, that, when *volume* is to be deduced from *volume*, the answer can be found by mere inspection of the equation according to the principles stated in § 26; and *thirdly*, that the rule on page 68 applies only to those problems in which *volume* is to be calculated from *weight*, or the reverse. In using this last rule it must be remembered that the "first substance" is always the one whose *weight* is given or sought, while the "second substance" is always the one whose *volume* is given or sought. It is evident, however, that the volume of any aeriform factor or product may also be found by dividing the weight in grammes — calculated by the rule of § 25 — by the known weight of one litre of the gas or vapor, and, on the other

hand, that, if the volume of the aeriform factor or product is first reduced to weight, the same simple rule may be used for calculating weight from volume.

In solving stochiometrical problems involving both weights and volumes, the last method will probably be preferred because it is the more obvious one, and it becomes therefore important to state in this connection how the weight in grammes of one litre of a gas or vapor may be found.

The weight in grammes of one litre of a gas or vapor, under the standard conditions of temperature and pressure, is, by [2],

$$W = 0.0896 \text{ Sp. Gr.},$$

or, since the specific gravity of a gas or vapor referred to hydrogen is approximately one half the molecular weight, we have also

$$W = 0.0896 \times \tfrac{1}{2} m.$$

When, therefore, either the specific gravity or the molecular weight of an aeriform substance is given, or when the symbol of the substance is known, from which we can of course at once determine the molecular weight, it is very easy to calculate the weight of one litre of the gas or vapor in grammes. In order to facilitate such calculations, we have given in Table III. the logarithms of the half-molecular weights of all the more common gases and vapors, and among the constant logarithms on the last page of the book will be found the logarithm of 0.0896, which is 8.9522. By adding this constant to the logarithms given in the table, we obtain in each case the logarithm of the weight of one litre of the gas or vapor named in grammes; that is,

$$\log W = 8.9522 + \log. \tfrac{1}{2} m.$$

Thus, for example, to find the weight of one litre of oxygen gas, we have

$$8.9522 + 1.2041 = 0.1563, \text{ the log. of } 1.433 \text{ grammes.}$$

When only approximate values are required, we may take the weight of a litre of hydrogen as $\frac{9}{100}$ of a gramme, and then most problems of this kind may be solved mentally.

By using logarithms in the solution of stochiometrical problems, the labor will be very greatly reduced, and we give an additional example of a problem involving both weights and volumes in order to show how the calculation is best arranged when made by the method last described.

Problem. How many litres of nitrous oxide gas can be made from 498.5 grammes of ammonic nitrate?

$$N_2H_4O_3 = 2\,H_2O + N_2O$$

	498.5 log.	2.6976
N_2O	46 log.	1.6628
$N_2H_4O_3$	80 ar. co. log.	8.0969
$\frac{1}{2}\,m$	32 ar. co. log.	8.4949
Constant	0.0896 ar. co. log.	1.0478
	Ans. 100 litres log.	2.0000

It must not be forgotten that in all such problems we assume that the gas volumes are measured under the standard conditions of temperature and pressure, and in the case of vapors this assumption sometimes involves the anomaly that the substance cannot retain its aeriform condition under such circumstances.

QUESTIONS AND PROBLEMS.

1. What is the molecular weight of plumbic sulphate, $Pb{=}O_2{=}SO_2$? Of ammonia alum, $(NH_4)_2$, $[Al_2]{\equiv}O_8{\equiv}(SO_2)_4$. $24H_2O$? Of calcic phosphate, $Ca_3{\equiv}O_6{\equiv}(PO)_2$? Ans. 303, 906.8, and 310.

2. What are the molecular weights of the symbols

$$3\,C_2H_4O_2 \qquad 5\,(FeSO_4.7\,H_2O) \qquad 7\,K_2{=}O_2{=}CO\,?$$

Ans. 180, 1390, and 967.4.

3. Are the total atomic weights of the two members of the following reaction equal?

$$Fe + (H_2SO_4 + Aq) = (FeSO_4 + Aq) + H{\cdot}H.$$

Ans. The total weight of each member of the equation is 154.

4. Calculate the percentage composition of ammonic chloride, NH_4Cl. Ans. Nitrogen, 26.17; Hydrogen, 7.48; Chlorine, 66.35.

5. Calculate the percentage composition of nitrobenzol, $C_6H_5NO_2$.

Ans. Carbon, 58.53; Hydrogen, 4.07; Nitrogen, 11.39; Oxygen, 26.01.

6. Given the percentage composition of chloroform as follows: Carbon, 10.04; Hydrogen, 0.83; Chlorine, 89.13. Required the symbol, knowing that the Sp. Gr. of chloroform vapor equals 59.75.

Ans. $CHCl_3$

7. Given the percentage composition of stanno-diethylic bromide as follows: Tin, 35.13; Carbon, 14.29; Hydrogen, 2.97; Bromine, 47.61. Required the symbols, knowing that the Sp. Gr. of the vapor equals 168. Ans. $SnC_4H_{10}Br_2$

8. Given the percentage composition of ethylene chloride as follows: Carbon, 24.24; Hydrogen, 4.04; Chlorine, 71.72. Required the symbol, knowing that the Sp. Gr. of the vapor equals 49.5.

Ans. $C_2H_4Cl_2$

9. Given the percentage composition of cream of tartar as follows: Potassium, 20.79; Hydrogen, 2.66; Carbon, 25.52; Oxygen, 51.03. Required the simplest symbol possible. Ans. $KH_5C_4O_6$

10. Given the percentage composition of crystallized ferrous sulphate as follows: Iron, 20.15; Sulphur, 11.51; Oxygen, 23.02; Water, 45.32. Required the simplest symbol possible.

Ans. Estimating the number of molecules of water (H_2O), as if water were a fourth element with an atomic weight of 18, we get $FeSO_4 . 7\,H_2O$.

11. The percentage composition of morphia according to Liebig's analysis is, — Carbon, 71.35; Hydrogen, 6.69; Nitrogen, 4.99; Oxygen (by loss), 16.97. What is the symbol of this alkaloid, and how closely does this symbol agree with the results of analysis?

Ans. The symbol $C_{17}H_{19}NO_3$ would require 71.58 Carbon, 6.66 Hydrogen, 4.91 Nitrogen, and 16.85 Oxygen.

12. It is required to find the weight of phosphorus in 155 kilo. of calcic phosphate ($Ca_3P_2O_8$). Ans. 31 kilo.

13. It is required to find the weight of sulphuric anhydride (SO_3) in 284 kilo. of sodic sulphate, Na_2SO_4. Ans. 160 kilo.

14. How many grammes of plumbic sulphate ($PbSO_4$) can be made from 2.667 grammes of sulphuric anhydride (SO_3)?

Ans. 10.1 grammes.

15. How many grammes crystallized cupric sulphate ($CuSO_4 . 5\ H_2O$) will yield 317 grammes of copper? Ans. 1,247 grammes.

16. Required the total molecular weight of crystallized sodic phosphate, knowing that 71.6 parts of the salt contain 9.2 parts of sodium, and that the total atomic weight of sodium in one molecule of the compound is 46. Ans. 358.

17. The molecular weight of potassic nitrate is 101.1, and 2.359 grammes of the salt contain 1.120 grammes of oxygen. What is the total atomic weight of oxygen, and also the number of oxygen atoms in one molecule?

Ans. Total atomic weight, 48. No. of oxygen atoms, 3.

18. How much nitric acid (HNO_3) is required to dissolve 3.804 grammes of copper (Cu), and how much cupric nitrate (CuN_2O_6) and how much nitric oxide (NO) will be formed in the process? The reaction is expressed by the equation

$$3\,Cu + (8\,HNO_3 + Aq) = (3\,CuN_2O_6 + 4\,H_2O + Aq) + 2\,\mathbb{NO}.$$

Ans. 10.08 grammes of nitric acid, 11.244 grammes of cupric nitrate, and 1.20 grammes of nitric oxide.

19. How much common salt ($NaCl$) must be added to a solution containing 30 grammes of argentic nitrate ($AgNO_3$) in order to throw down the whole of the silver, and how much argentic chloride ($AgCl$) will be thus precipitated?

$$(AgNO_3 + NaCl + Aq) = \mathbf{AgCl} + (NaNO_3 + Aq).$$

Ans. 10.32 grammes of salt, and 25.32 grammes of argentic chloride.

20. How many litres of ammonia gas ($\mathbb{NH}_3$) and how many of chlorine gas ($\mathbb{Cl}$-$\mathbb{Cl}$) are required to make one litre of nitrogen gas ($\mathbb{N}$-$\mathbb{N}$)? How many litres of hydrochloric acid gas ($\mathbb{HCl}$) are also formed?

$$2\,\mathbb{NH}_3 + 3\,\mathbb{Cl}\text{-}\mathbb{Cl} = 6\,\mathbb{HCl} + \mathbb{N}\text{-}\mathbb{N}.$$

Ans. 2 litres of ammonia gas, 3 litres of chlorine gas, and 6 litres of hydrochloric acid gas.

21. How many litres of hydrochloric acid gas (HCl) and how many of oxygen gas ($O{=}O$) can be obtained from one litre of aqueous vapor (H_2O), and how many litres of chlorine gas ($Cl{-}Cl$) must be used in the process?

$$2\,H_2O + 2\,Cl{-}Cl = 4\,HCl + O{=}O.$$

Ans. 2 litres of hydrochloric acid gas, ½ litre of oxygen gas, and 1 litre of chlorine gas.

22. How many litres of oxygen gas ($O{=}O$) are required to burn completely (i. e. to combine with) one litre of alcohol vapor (C_2H_6O), and how many litres of carbonic anhydride (CO_2) and how many of aqueous vapor (H_2O) are formed by the process? The chemical reaction which takes place when alcohol burns is expressed by the equation

$$C_2H_6O + 3\,O{=}O = 2\,CO_2 + 3\,H_2O.$$

Ans. 3 litres of oxygen gas, 2 litres of carbonic anhydride, and 3 litres of aqueous vapor.

23. How many litres of oxygen gas are required to burn one litre of arseniuretted hydrogen (H_3As), and how many litres of arsenious acid vapor (As_2O_3) and how many of aqueous vapor are formed in the process?

$$4\,H_3As + 6\,O{=}O = As_2O_3 + 6\,H_2O.$$

Ans. 1½ litres of oxygen gas, ½ litre arsenious acid vapor, and 1½ litres of aqueous vapor.

24. What is the weight of one litre of each of the undermentioned substances represented by the following symbols?

HCl	NH_3	NO	CO	CO_2	$CaCl_2$
Ans. 1.633,	0.761,	1.344,	1.354,	1.971,	3.139.

25. How many litres of chlorine gas can be made with 10.49 grammes of manganic oxide (MnO_2)?

$$MnO_2 + (4\,HCl + Aq) = (MnCl_2 + 2\,H_2O + Aq) + Cl{-}Cl.$$

Ans. 5 litres.

26. How many grammes of chalk ($CaCO_3$) are required to yield one litre of carbonic anhydride?

$$CaCO_3 + (2\,HCl + Aq) = (CaCl_2 + H_2O + Aq) + CO_2.$$

Ans. 4.46 grammes.

27. How many litres of hydrochloric acid gas (HCl) can be made with 8.177 kilogrammes of common salt ($NaCl$)?

$$(2\,NaCl + H_2SO_4 + Aq) = (Na_2SO_4 + Aq) + 2\,\mathbf{HCl}.$$

Ans. 3120 litres.

28. How many grammes of ferrous sulphide (FeS) are required to yield 568 $\overline{\text{c. m.}}^3$ of sulphuretted hydrogen (H_2S)?

$$\mathbf{FeS} + (H_2SO_4 + Aq) = (FeSO_4 + Aq) + \mathbf{H_2S}.$$

Ans. 2.24 grammes.

29. What is the proof that the symbol of water is H_2O? See analysis on page 9, and find vapor density in Table III.

30. What is the proof that the symbol of alcohol is C_2H_6O? that of acetic acid, $C_2H_4O_2$? that of ether, $C_4H_{10}O$?

CHAPTER VII.

CHEMICAL EQUIVALENCY.

27. **Chemical Equivalents.** — If in a solution of argentic sulphate we place a strip of metallic copper, we find after a short time that all the silver has separated from the solution, and that a certain quantity of copper has dissolved in its place.

$$(Ag_2SO_4 + Aq) + \mathbf{Cu} = (CuSO_4 + Aq) + \mathbf{Ag_2}. \qquad [30]$$

If now we pour off the solution of cupric sulphate, and place in this solution a strip of metallic zinc, the metallic copper in its turn will all separate, and to replace it a certain amount of zinc will dissolve.

$$(CuSO_4 + Aq) + \mathbf{Zn} = (ZnSO_4 + Aq) + \mathbf{Cu}. \qquad [31]$$

Lastly, if we pour off the solution of zincic sulphate, and place in this a strip of metallic magnesium, the zinc will in like manner be replaced by magnesium.

$$(ZnSO_4 + Aq) + \mathbf{Mg} = (MgSO_4 + Aq) + \mathbf{Zn}. \qquad [32]$$

In experiments like these, we can by proper analytical methods determine the relative quantities by weight of the several metals which thus replace each other, and we find that they are always the same. Thus, if our first solution contained 108 milligrammes of silver, the amount of each metal successively dissolved and precipitated would be, of copper, 31.7 m. g., of zinc, 32.6 m. g., of magnesium, 12 m. g. Moreover, if, instead of using in our experiments a metallic sulphate, we take a metallic chloride, nitrate, acetate, or any other compound of the metals, we find that the same definite ratios are preserved, at least in every case where the substitution is possible. It would appear then that these relative quantities of the several metals

exactly replace each other in all such cases. They are, therefore, regarded as the chemical equivalents of each other, in the sense that they are capable of filling each other's place.

In a strict sense, two quantities of different elements can be said to be *equivalent* only when they are actually capable of replacing each other in some known chemical reaction; but formerly the word was used with a much wider significance, and quantities of two different elements were said to be equivalent if they had been proved to be equivalent to the same quantity of some third element which served as a link of connection. In this way an equivalency may be established between all the chemical elements, and the old system of chemistry was based on a system of equivalency so determined. If the table of chemical equivalents on this old system is compared with a table of atomic weights on the new, it will be found that the numbers of the one are either the same as those of the other, or else some very simple multiples of them. The one set of numbers can be used in all stochiometrical calculations in the same way as the other, and on the old system the symbols stand for equivalents, as in the new they stand for atomic weights. The equivalents have this advantage, that they are the result of direct experiments, and are based on no hypothesis in regard to the molecular constitution of matter. But this hypothesis is necessary, in order to correlate a large number of facts which modern chemical investigation has brought to light, and when once made, the rest of the system follows as a necessary consequence.

28. **Quantivalence or Atomicity of the Elements.** — If now, starting with the atomic weights as they have been determined or assumed in Table II., we compare together the different elements from the point of view taken in the last section, it will be found that, while in some cases one atom of one element is the equivalent of one atom of another, in other cases it may be the equivalent of two, three, or four atoms. Since in the system of this book the symbols always stand for atomic weights, the relation here referred to is made evident whenever any metathetical reaction is expressed in the form of an equation. A

27.

In most cases, however, the quantivalence is indicated with sufficient clearness by the dashes which are used in this book to separate the parts of a molecular symbol. The number of these dashes is always the same as the quantivalence of the atoms, or groups of atoms, on either side.

With these additions to our notation we are able to express by our symbols all that was valuable in the old system of equivalents and at the same time all that is peculiar to our modern theories.

Precisely the same relations of quantivalence are manifested even more fully by the compound radicals, whenever in a chemical reaction they change places with elementary atoms, and their replacing value is indicated in the same way. Thus, in the following reaction,

$$\underset{\text{Acetylic Chloride.}}{\overset{\text{I}}{C_2H_3O}\text{-}Cl} + \underset{\text{Water.}}{H\text{-}O\text{-}H} = H\text{-}Cl + \underset{\text{Acetic Acid.}}{H\text{-}O\text{-}\overset{\text{I}}{C_2H_3O}} \qquad [36]$$

the radical C_2H_3O, named acetyl, changes places with one atom of hydrogen, and is therefore univalent, while in the next,

$$\underset{\text{Chloroform.}}{\overset{\text{III}}{C}H{=}Cl_3} + H_3N = 3\,HCl + \underset{\text{Hydrocyanic Acid.}}{\overset{\text{III}}{C}H{\equiv}N} \qquad [37]$$

the radical CH is as evidently trivalent.

The quantivalence of an element or radical is shown, not only by its power of replacing hydrogen atoms, but also by its power of replacing any other atoms whose quantivalence is known. Thus, as is shown by [30], the atom of copper is bivalent, because 63.4 m. c. of this metal, the weight of one atom, replaces 216 m. c. of silver, which is the weight of two atoms, and these last by [33] are known to be univalent. Again, it is shown by [31] that the atoms of zinc are bivalent, because 65.2 m. c. of zinc, or one atom, replace 63.4 m. c. of copper, the weight of an atom just shown to be bivalent.

Moreover, it is a remarkable fact, which has a most important bearing on our chemical philosophy, that the quantivalence of an element or radical, as shown by its replacing power, corresponds exactly to what we may term its *atom-fixing power*, that is, to its power of holding other elements or radicals in a

molecule. We may take as examples the molecules of four very characteristic compounds, namely, hydrochloric acid, water, ammonia, and marsh gas, whose symbols may be written thus:—

$$\overset{\text{I}}{H}\text{-}\overset{\text{I}}{Cl} \qquad \overset{\text{I}}{H}\text{-}\overset{\text{II}}{H}\text{-}\overset{\text{I}}{H} \qquad \overset{\text{I}}{H}\text{-}\overset{\text{I}}{H}\text{-}\overset{\text{I}}{H}\text{-}\overset{\text{III}}{N} \qquad \overset{\text{I}}{H}\text{-}\overset{\text{I}}{H}\text{-}\overset{\text{I}}{H}\text{-}\overset{\text{IV}}{C}\text{-}\overset{\text{I}}{H}$$

Hydrochloric Acid. Water. Ammonia. Marsh Gas.

By these symbols it appears that, while the univalent atom of chlorine can hold but one atom of hydrogen, the bivalent atom of oxygen holds two, the trivalent atom of nitrogen three, and the quadrivalent atom of carbon four atoms of the same element. It appears, then, that the Roman numerals or dashes, which represent the replacing power of the atoms or radicals, represent also the *atom-fixing power* of the same, measured in each case by the number of atoms of hydrogen, or their equivalents, with which these atoms or radicals can combine to form a single molecule. On account of the importance of this principle we shall extend our illustrations to a number of other compounds, and the student should carefully compare in each case the quantivalence on the two sides of the dash or dashes, which mark the atom-fixing power of the dominant atom in the molecule.

$$\overset{\text{I}}{Na}\text{-}\overset{\text{I}}{Cl} \qquad \overset{\text{I}}{K}\text{-}\overset{\text{I}}{I} \qquad \overset{\text{I}}{C_2H_5}\text{-}\overset{\text{I}}{Br} \qquad \overset{\text{I}}{K}\text{-}\overset{\text{I}}{C}\text{N}$$

Sodic Chloride. Potassic Iodide. Ethylic Bromide. Potassic Cyanide.

$$\overset{\text{I}}{K}\text{-}\overset{\text{II}}{O}\text{-}\overset{\text{I}}{H} \qquad \overset{\text{II}}{Pb}\text{=}\overset{\text{II}}{O} \qquad \overset{\text{I}}{H}\text{-}\overset{\text{II}}{O}\text{-}\overset{\text{I}}{NO_2} \qquad \overset{\text{I}}{H}\text{-}\overset{\text{II}}{O}\text{-}\overset{\text{I}}{C_2H_3O};$$

Potassic Hydrate. Plumbic Oxide. Nitric Acid. Acetic Acid.

$$\overset{\text{I}}{H}\text{-}\overset{\text{I}}{H}\text{-}\overset{\text{I}}{C_2H_5}\text{=}\overset{\text{III}}{N} \qquad (\overset{\text{I}}{C_2H_5})_3\text{=}\overset{\text{III}}{P} \qquad \overset{\text{I}}{CH_3}\text{-}\overset{\text{I}}{C_2H_5}\text{-}\overset{\text{I}}{C_5H_{11}}\text{=}\overset{\text{III}}{N}$$

Ethylamine. Triethyl-phosphine. Methyl-ethyl-amyl-amine.

The quantivalence of the chemical elements, especially as indicated by their atom-fixing power, is by no means always the same. They constantly exhibit under different conditions an unequal atom-fixing power. Thus we have

$$\overset{\text{II}}{Sn}\overset{\text{IV}}{Cl_4} \text{ and } \overset{\text{IV}}{Sn}\overset{\text{II}}{Cl_2} \qquad \overset{\text{III}}{P}\overset{\text{V}}{Cl_5} \text{ and } \overset{\text{III}}{P}\overset{\text{V}}{Cl_3} \qquad \overset{\text{III}}{N}\overset{\text{V}}{H_4}\overset{\text{V}}{Cl} \text{ and } \overset{\text{III}}{N}\overset{\text{V}}{H_3}$$

$$\overset{\text{II}}{Os}\overset{\text{VIII}}{O_4} \qquad \overset{\text{IV}}{Os}\overset{\text{II}}{Cl_2} \qquad \overset{\text{VIII}}{Os}\overset{\text{IV}}{Cl_4} \qquad \overset{\text{VIII}}{Os}\overset{\text{II}}{O_4} \qquad \overset{\text{II}}{Fe}\overset{\text{VI}}{Cl_2} \qquad \overset{\text{VI}}{Fe_2}\overset{\text{II}}{Cl_6}.$$

[illegible] different conditions of quantivalence the same element [illegible]lds compounds which differ from each other as widely

as the compounds of different elements, and hence arises a great difficulty in classifying the elements, for the same element in different states of quantivalence may have wholly different affinities and relations. Thus the *ferrous* compounds of iron which contain $\overset{II}{Fe}$ are wholly unlike the *ferric* compounds which contain $[\overset{VI}{Fe_2}]$; and while in the first state iron is closely related to magnesium, in the last state it must be classed with aluminum. A still more striking example is offered by the element manganese, which in its extreme conditions of quantivalence is related to elements as unlike each other as zinc and chlorine. As a general rule, however, one of the possible conditions of an element is more common and stable than the rest, and in several cases, as with hydrogen, the quantivalence appears to be absolutely invariable. A multitude of facts illustrating these principles will be brought to notice in Part II. of this work.

The possible degrees of quantivalence of an elementary atom are usually related to each other by a very simple law. With few exceptions they are either all even or all odd. Thus the atom of sulphur may be sextivalent, quadrivalent, and bivalent, but is never trivalent or univalent; and, on the other hand, the atom of nitrogen may be quinquivalent, trivalent, and univalent, but not quadrivalent or bivalent. Atoms like those of sulphur, which have even degrees of quantivalence, have been called *artiads*, while those having odd degrees, like nitrogen, have been called *perissads*. This distinction has been thought to be one of fundamental importance; but although the principle in general holds true, there are striking exceptions which have not yet been reconciled with the theory.

The word *atomicity* is used by some authors to express essentially the same atomic relations which we have called quantivalence, and atoms are classed as monads, dyads, triads, etc., according to the number of univalent atoms they replace or bind together. These terms are in themselves unobjectionable, but they are usually associated with a theory still held by some chemists, that every atom has a fixed and invariable atomicity which is its essential characteristic. Those who adopt this theory

...ENCE OF RADICALS.

...we have referred to variable qua...
...and artifices, forgetting that t...
...is to classify facts, and that it h...
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...Quantivalence of Radicals. — When in th...
...dominant or central atom i...
...as it can hold of that kind, th...

$$H_4C \qquad H_4N \qquad H_4C$$

...although nitrogen is quinqui-
...the intervention of some other atom
...three atoms of hydrogen. While, on

$$\overset{\text{IV}}{C}O_2 \qquad \overset{\text{IV}}{P}O_2 \qquad \overset{\text{IV}}{S}nCl_2$$

...combine directly with more oxygen
...the saturated molecules

$$CO_2 \qquad PO_5 \qquad SnCl_4.$$

...a saturated molecule we withdraw one or more
...hydrogen, or their equivalents, *the rest may be re-*
...*compound radical with an atomicity equal to the*
...*hydrogen atoms, or their equivalents, withdrawn.* Thus,
...the saturated molecule of marsh gas H_4C we withdraw
...hydrogen, we get the radical methyl H_3C, which is
...we withdraw two atoms, we have the radical H_2C,
...if we withdraw three, there results HC, which
...if we withdraw all four, we fall back on
...atom of carbon. Again, if from the saturated mole-
...we withdraw one atom of the dyad
...two atoms of NO_2, each of which is a

nomad.* If now we withdraw from NO_2 one of its remaining atoms of oxygen, we have left NO, which is a triad. Lastly, a molecule of sulphuric anhydride, SO_3, which is saturated, gives, by withdrawing one atom of oxygen, SO_2, which acts as a bivalent radical. These considerations lead us to a simple rule, first stated by Wurtz, which in almost every case will enable us to infer the atomicity of any given radical: *The atomicity of a compound radical is always equal to the number of hydrogen atoms, or their equivalents, which the rest may be regarded as having lost.*

It must not be supposed, however, that all such radicals are possible compounds. In a few cases only these rests, of which we have been speaking, form non-saturated molecules, which are capable of existing in a free state, like those of carbonic oxide, nitric oxide, and sulphurous oxide. At other times they are compound radicals, which, *by doubling*, form molecules that can exist in a free state, as those of cyanogen gas, and perhaps also of some hydrocarbons. Again, they appear as compound radicals, which pass and repass in so many chemical reactions as to almost force upon us the belief that they have a real existence, and represent the actual grouping of the atoms in the compounds of which they seem to be an integral part. Still again, and even more frequently, they can only be regarded as convenient factors in a chemical equation.

QUESTIONS AND PROBLEMS.

1. Analyze the following metathetical reactions, showing in each case how many parts of the several elements are equivalent to one part by weight of hydrogen, and also to how many atoms of hydrogen one atom of each of the interchanging elements corresponds. For the atomic weights refer to the table on page 266.

* As in many of its chemical relations a compound radical is the equivalent of an elementary atom, it is usual to speak of *atoms of a radical*, although the usage implies an obvious solecism.

explain the phenomena which we have referred to variable quantivalence by various assumptions and artifices, forgetting that the whole object of such a theory is to classify facts, and that it has outlived its usefulness as soon as it becomes necessary to resort to expedients to bring the facts under its control. We therefore prefer the term *quantivalence* and its derivatives, which imply no theory, and we shall use the terms *atomicity*, *monads*, *dyads*, etc., only in such cases as those described in the next section, where the quantivalence is invariable.

29. **Atomicity or Quantivalence of Radicals.** — When in the molecule of any compound the dominant or central atom is united to as many other atoms as it can hold of that kind, the molecule is said to be saturated; thus,

$$HCl \qquad H_2O \qquad H_3N \qquad H_4C$$

are all saturated molecules; for, although nitrogen is quinquivalent, it cannot, without the intervention of some other atom or radical, hold more than three atoms of hydrogen. While, on the other hand, the molecules

$$\overset{\text{II}}{CO} \qquad \overset{\text{II}}{PCl_3} \qquad \overset{\text{II}}{SnCl_2}$$

are not saturated, for they can combine directly with more oxygen or chlorine, forming thus the saturated molecules

$$CO_2 \qquad PCl_5 \qquad SnCl_4.$$

If now from a saturated molecule we withdraw one or more atoms of hydrogen, or their equivalents, *the rest may be regarded as a compound radical with an atomicity equal to the number of hydrogen atoms, or their equivalents, withdrawn.* Thus, if from the saturated molecule of marsh gas H_4C we withdraw one atom of hydrogen, we get the radical methyl H_3C, which is a monad; if we withdraw two atoms, we have the radical H_2C, which is a dyad; if we withdraw three, there results HC, which is a triad; and lastly, if we withdraw all four, we fall back on the tetrad atom of carbon. Again, if from the saturated molecule of nitric anhydride N_2O_5 we withdraw one atom of the dyad oxygen O, it falls into two atoms of NO_2, each of which is a

nomad.* If now we withdraw from NO_2 one of its remaining atoms of oxygen, we have left NO, which is a triad. Lastly, a molecule of sulphuric anhydride, SO_3, which is saturated, gives, by withdrawing one atom of oxygen, SO_2, which acts as a bivalent radical. These considerations lead us to a simple rule, first stated by Wurtz, which in almost every case will enable us to infer the atomicity of any given radical: *The atomicity of a compound radical is always equal to the number of hydrogen atoms, or their equivalents, which the rest may be regarded as having lost.*

It must not be supposed, however, that all such radicals are possible compounds. In a few cases only these rests, of which we have been speaking, form non-saturated molecules, which are capable of existing in a free state, like those of carbonic oxide, nitric oxide, and sulphurous oxide. At other times they are compound radicals, which, *by doubling*, form molecules that can exist in a free state, as those of cyanogen gas, and perhaps also of some hydrocarbons. Again, they appear as compound radicals, which pass and repass in so many chemical reactions as to almost force upon us the belief that they have a real existence, and represent the actual grouping of the atoms in the compounds of which they seem to be an integral part. Still again, and even more frequently, they can only be regarded as convenient factors in a chemical equation.

QUESTIONS AND PROBLEMS.

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* As in many of its chemical relations a compound radical is the equivalent of an elementary atom, it is usual to speak of *atoms of a radical*, although the usage implies an obvious solecism.

$$\underset{\text{Alcohol.}}{2\,H\text{-}O\text{-}C_2H_5} + \underset{\text{Potassium.}}{K\text{-}K} = \underset{\text{Potassic Ethylate.}}{2\,K\text{-}O\text{-}C_2H_5} + H\text{-}H.$$

$$\underset{\text{Water.}}{2\,H\text{-}O\text{-}H} + Mg = \underset{\text{Magnesic Hydrate.}}{Mg{=}O_2{=}H_2} + H\text{-}H.$$

$$\underset{\text{Antimonious Hydrate.}}{Sb{=}O_3{=}H_3} + 3\,HCl = \underset{\text{Antimonious Chloride.}}{SbCl_3} + 3\,H\text{-}O\text{-}H.$$

$$4\,H\text{-}O\text{-}H + \underset{\text{Silicic Chloride.}}{SiCl_4} = \underset{\text{Silicic Acid.}}{H_4{=}O_4{=}Si} + 4\,HCl.$$

2. Make out a table of chemical equivalents so far as the reactions of this chapter will enable you to deduce them from the atomic weights given in Table II.

3. Analyze the following metathetical reactions, showing in each case how the quantivalence of the several compound radicals involved in the metathesis is indicated.

$$\underset{\text{Water.}}{H\text{-}O\text{-}H} + \underset{\text{Acetic Ether.}}{(C_2H_3O)\text{-}O\text{-}(C_2H_5)} = \underset{\text{Acetic Acid.}}{(C_2H_3O)\text{-}O\text{-}H} + \underset{\text{Alcohol.}}{H\text{-}O\text{-}(C_2H_5)}$$

$$\underset{\text{Potassic Cyanide.}}{2\,K\text{-}(CN)} + \underset{\text{Ethylene Bromide.}}{(C_2H_4){=}Br_2} = \underset{\text{Ethylene Cyanide.}}{(C_2H_4){=}(CN)_2} + \underset{\text{Potassic Bromide.}}{2\,KBr}$$

$$\underset{\text{Water.}}{3\,H\text{-}O\text{-}H} + \underset{\text{Glyceryllic Chloride.}}{(C_3H_5){\equiv}Cl_3} = \underset{\text{Glycerine.}}{(C_3H_5){\equiv}O_3{=}H_3} + \underset{\text{Hydrochloric Acid.}}{3\,HCl}$$

The names of the radicals are as follows: C_2H_3O, Acetyl; C_2H_5, Ethyl; C_2H_4, Ethylene; C_3H_5, Glyceryl; CN, Cyanogen.

4. What is the atom-fixing power or quantivalence of the different atoms and radicals in the following symbols?

$$\underset{\text{Potassic Sulphantimonite.}}{K_3{=}S_3{=}SbS} \qquad \underset{\text{Acid Sodic Carbonate.}}{H.Na{=}O_3{=}CO} \qquad \underset{\text{Ammonic Nitrite.}}{(NH_4)\text{-}O\text{-}NO}$$

$$\underset{\text{Oxamide.}}{H_2{=}N_2{=}C_2O_2} \qquad \underset{\text{Succinamic Acid.}}{(HO)_1(H_2N){=}(C_4H_4O_3)} \qquad \underset{\text{Tartar Emetic (dried).}}{K.Sb{=}O_1C_4H_2O_4}$$

5. If H_2O; C_2H_6; C_2H_6O (alcohol); $COCl_2$ (phosgene gas); $C_2H_4O_2$ (acetic acid), and $C_2H_2O_4$ (oxalic acid) are saturated molecules, what is the atomicity of the radicals HO (hydroxyl); C_2H_5 (ethyl); C_2H_4 (ethylene); C_2H_4O (aldehyde); CO (carbonyl); C_2H_3O (acetyl), and C_2O_2 (oxatyl)?

CHAPTER VIII.

STRUCTURE OF MOLECULES.

30. **Substitution.** — When acetic acid is exposed to the action of chlorine gas, we obtain three successive products, which, although not greatly differing from the original compound in their chemical relations, are found on analysis to have lost a certain amount of hydrogen, and to have gained an equivalent amount of chlorine in its place. These products are, —

Acetic Acid,	$C_2H_4O_2$	or	$(C_2H_3\overset{I}{O})\text{-}\overset{II}{O}\text{-}\overset{I}{H}$
Chloracetic Acid,	$C_2(H_3Cl)O_2$	"	$(C_2H_2Cl\overset{I}{O})\text{-}\overset{II}{O}\text{-}\overset{I}{H}$
Dichloracetic Acid,	$C_2(H_2Cl_2)O_2$	"	$(C_2HCl_2\overset{I}{O})\text{-}\overset{II}{O}\text{-}\overset{I}{H}$
Trichloracetic Acid,	$C_2(HCl_3)O_2$	"	$(C_2Cl_3\overset{I}{O})\text{-}\overset{II}{O}\text{-}\overset{I}{H}$

As the symbols indicate, we are thus able to replace either one, two, or three of the four atoms of hydrogen which the molecule of acetic acid contains by atoms of chlorine. We cannot, however, thus replace the fourth atom; and this fact seems to prove that there is a real difference between this atom of hydrogen and the other three; that is, that it stands in a different relation to that atomic structure which we call a molecule of acetic acid. This difference we attempt to represent by the symbols in the second column of the table just given; and although the student will not as yet comprehend the full meaning of these symbols, he can easily see that they represent the three replaceable hydrogen atoms as standing in a different relation to the molecule from that of the fourth. Moreover, since all of these products resemble the original substance in that they yield, when treated with alkalies, crystalline salts in which the

fourth atom of hydrogen is replaced by an atom of sodium, potassium, or ammonium, as the case may be, it is also evident that the chemical relations of these compounds must depend to a large extent on the manner in which the atoms are combined, and not simply on the qualities or proportions of the elementary substances present in the compound.

Products which sustain a similar relation to the compound from which they are derived are called *substitution products*, and it was the study of such substances that first led Dumas to the conception of what he called *chemical types;* and this term as first used was intended to convey the idea just expressed without defining the mode of combination. It had previously been assumed that the qualities and relations of a compound depended solely on the nature and proportions of its constituents, and this conception of structure opened a new, and, as has proved, a most fruitful field of chemical investigation.

31. **Isomorphism.** — Closely associated with the facts of the last section, which find their chief manifestation in substances of organic origin, are the phenomena of isomorphism, which are equally conspicuous among artificial salts and native minerals.

Fig. 1.

There seems to be an intimate connection between chemical composition and crystalline form, and two substances which under a like form have an analogous composition are said to be *isomorphous.* Thus the following minerals all crystallize in rhombohedrons (Fig. 1), which have very nearly the same interfacial angles, and, as the symbols show, they have an analogous composition. They are therefore isomorphous.

Calcic Carbonate, or Calcite,	$Ca{\cdot}CO_3$
Magnesic Carbonate, or Magnesite,	$Mg{\cdot}CO_3$
Ferrous Carbonate, or Chalybdite,	$Fe{\cdot}CO_3$
Manganous Carbonate, or Diallogite,	$Mn{\cdot}CO_3$
Zincic Carbonate, or Smithsonite,	$Zn{\cdot}CO_3$

The most cursory examination of these symbols will show that they differ from each other only in the fact that one metallic

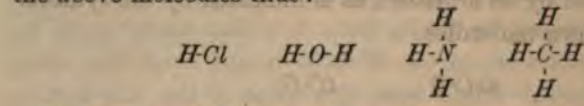
atom has been replaced by another. It is not, however, every metallic atom which can thus be put in without altering the form. This is a peculiarity that is confined to certain groups of elements, which for this reason are called groups of isomorphous elements. Moreover, as a rule, there is a close resemblance between the members of any one of these groups in all their other chemical relations. These facts, like those of the last section, tend to show that the molecules of every substance have a determinate structure, which admits of a limited substitution of parts without undergoing essential change, but which is either destroyed or takes a new shape when in place of one of its constituents we force in an unconformable element. A well-known class of artificial salts, called the alums, affords even a more striking illustration of the principles of isomorphism than the simpler example we have chosen; but all the bearings of the subject cannot be understood without a knowledge of crystallography, and we must therefore refer for further details to works on mineralogy.

32. **Dominant Atoms.** — Assuming that the weights of the atoms have been previously established by the methods of Chapter IV., it has been shown in Chapter VII. that the quantivalence of an atom is a fact of observation. When now we add to this the further fact, that the quantivalence of an atom is the measure of what we have called its atom-fixing power, we are naturally brought to the conclusion that these phenomena are merely different manifestations of the same attribute of the elementary atoms by virtue of which each is able to bind to itself a limited number only of other atoms. Thus in the molecules represented by the symbols

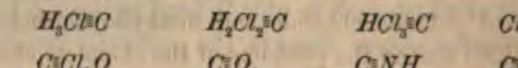
$$\overset{\text{I}}{HCl} \qquad \overset{\text{II}}{H_2O} \qquad \overset{\text{III}}{H_3N} \qquad \overset{\text{IV}}{H_4C}$$

in which the number of univalent hydrogen atoms indicates the known quantivalence of the atoms with which they are associated, we must regard these hydrogen atoms, not as united with each other, but as severally bound to what we may call the *dominant atom* of the group. It appears as if each atom had a certain definite number of poles or points, at which other atoms can be

united with it, and that its possibilities of combination are limited by the number of these *bonds*. Conventionally we represent these bonds by dashes, and indicate the constitution of the above molecules thus :—



It will be noticed that the conclusion, simple as it is, which we have now reached, necessarily involves the same idea of molecular structure already recognized in the previous sections. We do not as yet assert in regard to these hydrogen atoms that they are united to the *dominant atom* of the molecule in any definite relative position, and the configuration of our symbol is purely fanciful. Indeed, we do not necessarily conceive that the atoms of a molecule have any fixed relative position; and there are phenomena which would lead us to infer that they may be in motion among themselves. But we do feel justified in the conclusion, that, in the molecules above represented, the hydrogen atoms are directly united to the dominant atom which forms the nucleus of the group, and that they are not united to each other. These conclusions, moreover, are greatly confirmed by the fact, that, when the hydrogen atoms of these molecules are replaced by atoms of a different kind, it is always the case that, while a univalent atom takes the place of a single hydrogen atom, a bivalent atom replaces two, a trivalent atom three, and a quadrivalent atom four such atoms. Thus we have



It is not easy to form a clear conception of the mode of action of the force which determines such definite bonds of union between various atoms. The nearest analogy to these remarkable phenomena is that presented by multiple magnetic poles, and there are facts which suggest the idea that the chemical force which binds together the atoms is a polar force. In harmony with this conception is the fact already referred to, that the different degrees of quantivalence of the same atom differ in most

cases, if not always, by pairs. In such cases the unused bonds or poles of the dominant atom may be supposed to neutralize each other, like two opposite poles of a magnet when brought in contact or united by an armature, as is indicated by the symbols of two well-known molecules,

$$O{=}C{=}O \qquad C{\equiv}O.$$

When to each of the bonds of a multivalent radical is united an atom of the same kind, as for example in the molecules H_2O and H_4C, we cannot — at present at least — distinguish one from the other, and the forces exerted at the several points appear to be in all respects equal; but when the atoms united to the nucleus are not all alike, then at once a marked difference becomes manifest. Thus in the molecules $K{-}O{-}H$ and $H_3{-}C{-}Cl$ we are able to prove that the atom of potassium in the first case, and the atom of chlorine in the second, stand in a very different relation to the nucleus of the molecule from that sustained by the several atoms of hydrogen.

33. **Evidence furnished by Chemical Reactions.** — Having established in the last section the fundamental facts in relation to the structure of molecules, we are now prepared to understand the manner in which our knowledge of this subject has been extended by the evidence of chemical reactions.

According to Berthelot, when methylic chloride is acted on by a boiling solution of potassic hydrate (substances whose symbols, H_3CCl and KOH, were given above), the two well-known compounds named potassic chloride and methylic alcohol can readily be identified among the products of the chemical change. In regard to the molecular weights of these substances there is no question, and from these weights, in connection with the percentage composition of the compounds furnished by analysis, we at once deduce by § 24 the symbols KCl and CH_4O. Now in regard to the structure of the first molecule there can be no question. It consists solely of two univalent atoms, and so far as relative position is concerned these can only be arranged in one way. Then, with the facts already known, we can write the reaction of the process just described thus: —

$$H_3C\text{-}Cl + K\text{-}O\text{-}H = K\text{-}Cl + H_3C\text{-}O\text{-}H;$$

when it becomes evident that the atom of potassium has changed place with the radical H_3C, and hence that the structure of the molecule of methylic alcohol must be

$$\begin{array}{c} H \\ | \\ H\text{-}C\text{-}O\text{-}H, \\ | \\ H \end{array}$$

at least so far as the structure is represented when the relative order in which the atoms are united is indicated.

Again, if potassic hydrate is gently heated in an atmosphere of carbonic oxide, CO, a slow but regular absorption of the gas takes place, and a well-known salt, called potassic formiate, results. As the molecular weight and percentage composition of this product are well known, there is no question about its symbol, and we can write the reaction by which it is formed thus:—

$$K\text{-}O\text{-}H + CO = K\text{-}O\text{-}COH.$$

If now we take into account the known quantivalence of the several atoms, and also the facts which will appear hereafter, that both in carbonic oxide and in potassic hydrate the oxygen atoms are united to the potassium and carbon atoms, respectively, by a force so powerful that these atoms could not have been parted under the conditions of the experiments, we find that there is but one order in which the atoms of the product can be grouped. This order is shown by the following symbol:—

$$\begin{array}{c} O \\ \| \\ K\text{-}O\text{-}C\text{-}H. \end{array}$$

It will be noticed that, while in this group the potassium and carbon atoms remain in their old associations, the quantivalence of all the atoms is satisfied.

If now we distil with sulphuric acid potassic formiate, the substance obtained in the last reaction, the product is a volatile liquid called formic acid, which, when pure, is known to have the composition and molecular weight indicated by the symbol

H_2O_2C. This substance, when treated with potassic hydrate, gives us again potassic formate; and the only other product of the reaction is water. Hence the reaction must be

$$K\text{-}O\text{-}H + H_2O_2C = H\text{-}O\text{-}H + K\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}H$$

and it at once becomes evident that the structure of the molecule of formic acid is represented by the symbol

$$H\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}H$$

and that the atom of hydrogen, which has changed place with the atom of potassium in this reaction, is the one which is united to the atom of oxygen, and not the one united to the atom of carbon.

Comparing now the structure of formic acid with that of methylic alcohol,

$$H\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \qquad H\text{-}O\text{-}\overset{\overset{H}{|}}{C}\text{-}H,\ \overset{H}{|}$$

Formic Acid. Methylic Alcohol.

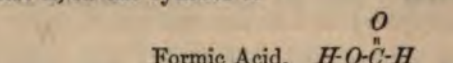
we see at once that the only difference is, that in the first an atom of oxygen has the place of two of the hydrogen atoms, which are united to the carbon nucleus in the last.

Formic acid and methylic alcohol are the first members of two parallel series of compounds, of which only the four succeeding members in each series are given in the following table.

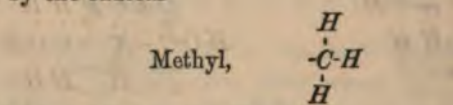
Formic Acid,	$H\text{-}O\text{-}CHO$	Methylic Alcohol,	$H\text{-}O\text{-}CH_3$
Acetic Acid,	$H\text{-}O\text{-}C_2H_3O$	Ethylic Alcohol,	$H\text{-}O\text{-}C_2H_5$
Propionic Acid,	$H\text{-}O\text{-}C_3H_5O$	Propylic Alcohol,	$H\text{-}O\text{-}C_3H_7$
Butyric Acid,	$H\text{-}O\text{-}C_4H_7O$	Butylic Alcohol,	$H\text{-}O\text{-}C_4H_9$
Valerianic Acid,	$H\text{-}O\text{-}C_5H_9O$	Amylic Alcohol,	$H\text{-}O\text{-}C_5H_{11}$

In order to interpret the structure of these compounds, we have, in the first place, the fact, that from each one of the acids we can form a compound with potassium by a reaction in every respect similar to that by which potassic formiate was obtained

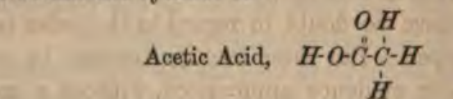
above. Moreover, each acid is related to the corresponding alcohol in the same way that formic acid is related to methylic alcohol. Hence we conclude that the structure of all these compounds, both acids and alcohols, is at least so far similar that it may be represented in every case by the general symbol $H\text{-}O\text{-}R$, in which R stands for a *compound radical* (§ 23) differing in each compound. Moreover, in regard to these compound radicals, we know that the radical of the acid differs from the radical of the alcohol only in that the former contains an atom of oxygen in place of two atoms of hydrogen in the latter. Comparing next the radicals themselves, with a view of discovering the structure of this portion of the several molecules, we notice that each one differs from that which follows next in the series by CH_2, and hence that if, in the symbol of



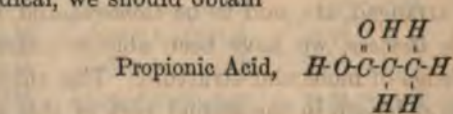
we replace the hydrogen atom, which is united to the carbon nucleus by the radical



we shall obtain the symbol of



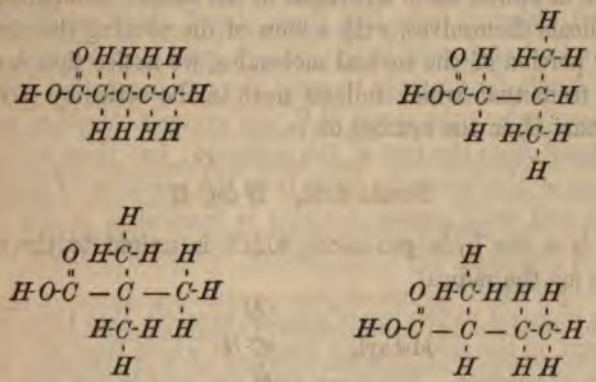
Replacing a corresponding hydrogen atom of acetic acid by the same radical, we should obtain



We may conceive that each successive member of the series might be thus obtained. Moreover, the successive alcohols might be derived in a similar way; and it is obvious that the theory of the structure of these compounds, which this possible mode of derivation suggests, satisfies all the conditions which the quantiva-

lence of the several atoms requires. Now it is possible to derive each of the radicals we have been considering from the one next above it in the same series, by such substitutions as we have indicated; and even if this cannot be done with these actual alcohols and acids, it can be done with compounds derived from them, in which the same radicals can be shown to exist.

The symbol of valerianic acid can be arranged in four ways, in all of which the quantivalence of the several atoms is satisfied, thus: —



Now these four symbols correspond to four different compounds whose reactions leave no doubt in regard to the order in which the atoms are grouped. But these reactions cannot be rendered intelligible, nor their evidence appreciated, without a more extended knowledge of chemical facts than can here be assumed. Compounds like the last, whose molecules consist of the same atoms differently arranged, are said to be *isomeric*, and, through the study of such *isomers*, we have been able to extend very greatly our knowledge of molecular structure. This subject will be developed more at length in the second part of this work, in connection with the compounds of carbon. Our only object in this place is to explain what is meant by molecular structure, and to indicate the course of reasoning by which we seek to establish it.

34. **Structural or Graphic Symbols.** — Chemical formulas, like those of the last few sections, by which we seek to indicate the

order in which the atoms are united, and hence, also, the manner in which a complex molecule may break up, are called sometimes *structural* and sometimes *graphic symbols*, and are to be distinguished from the simpler symbols used earlier in the book, which express only the relative proportions in which the elements are combined, and which, since they are simply expressions of the results of analysis on a concerted plan, are called *empirical symbols*. Whether these graphic symbols can be regarded in any sense as indicating the actual grouping of the material atoms is very doubtful, although facts like those stated above would seem to indicate that such may be the case, at least to a limited extent. It is difficult, for example, to resist the conclusion that in alcohol and its congeners the atoms C_2H_5 are grouped together in some sense apart from the rest of the molecule; but then we have no evidence of this grouping apart from the reactions of these compounds, and, until greater certainty is reached, it is not best to attach a significance to our symbols beyond the truths they are known to illustrate.

It is objected to the use of graphic symbols, that they bias the judgment on the side of some theory, of which they are more or less the exponents. But when they are used in the sense stated above, this objection has no force, for the reactions they prefigure are no less facts than the definite proportions they conventionally represent. Moreover, as science advances, we have every reason to believe that we shall gain more and more knowledge of the actual relations between the parts of a material molecule; and, as has already been intimated, there can hardly be a doubt that in some cases our graphic symbols do express even now actual knowledge of this sort, however crude and partial it may be. Our present graphic symbols are indeed the expressions of partial generalizations, which, however imperfect, have an element of truth. Hence it is that they have pointed out new lines of investigation, have led to new discoveries, and have been of the greatest value to science. They will doubtless soon be superseded by other graphic symbols, expressing other partial generalizations, to serve the same purpose in their turn, and be likewise forgotten. We must not, however, despise these temporary ex-

pedients of science. They are not only useful, but necessary, and cannot mislead the student if he remembers that all such aids are merely the scaffoldings around the science, on which the builders work. It is from this point of view alone that we are to look at the whole idea of chemical atoms, which lies at the basis of our modern chemical philosophy. That this idea is actually realized in the concrete form which it takes in some minds, can hardly be believed. The true chemical idea of the *atom* is more nearly represented by the corresponding Latin word *individuum*. The atom is the chemical individual, the unit, in which the mind seeks to repose for the time the individuality of that as yet undivided substance we call an element.

Various methods of writing structural symbols are employed by chemists, but these are usually such obvious applications of the principles we have discussed that they require no detailed description. To save space and labor in printing, we have adopted in this book a linear form, using dashes only so far as is necessary to indicate those relations of the parts of a complex molecule to which we wish to call attention. The subject has been so far developed that the structure of the ordinary radicals, such as methyl, ethyl, hydroxyl, cyanogen, ammonium, etc., may be regarded as established; and as a rule, therefore, it is not necessary to indicate their structure in writing the symbols of the complex molecules of which these radicals may form a part. Thus, the structure of the four valerianic acids is sufficiently indicated by the following formulæ: —

Normal Valerianic Acid,	$H\text{-}O\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
Ordinary Valerianic Acid,	$H\text{-}O\text{-}CO\text{-}CH_2\text{-}CH(CH_3)_2$
Trimethyl-acetic Acid,	$H\text{-}O\text{-}CO\text{-}C(CH_3)_3$
Methyl-ethyl-acetic Acid,	$H\text{-}O\text{-}CO\text{-}CH(CH_3)(C_2H_5)$

in which, as will be seen, commas are used to separate the radicals which are united to the same dominant atom. Notice that the radicals separated by commas are not united among themselves, and that the dominant atom to which they are severally bound is indicated by the dashes which precede or follow the symbols isolated by the punctuation marks.

35. **Unitary Theory.** — The comparatively recent conception that a molecule is a complex unit all of whose parts are bound together by atomic bonds, is frequently called the *unitary theory*, in contradistinction to the *dualistic theory* on which the older system of chemistry was based. Modern chemical philosophy is an outgrowth of the unitary theory, but the student should not fail to make himself acquainted with the system which preceded it, and which served the purpose of a rapidly growing science for more than fifty years. Indeed, it is very important that every student of science should learn the history of scientific theories, for otherwise he cannot properly appreciate the true relations of the theories of his own time, and is in danger of mistaking hypotheses for facts.*

Before closing this chapter, it remains to mention a few consequences of the unitary theory, which, although almost self-evident, might be overlooked if not dwelt upon specially.

In the first place it is evident that the integrity of every complex molecule depends upon the multivalence of one or more of its atoms. These multivalent atoms act as so many atomic clamps to bind univalent atoms together. Moreover, the whole virtue of a compound radical consists in the circumstance that it is an incomplete structure of the same sort, and its quantivalence is in every case equal to the number of univalent atoms (or their equivalents) which are required to complete it, or which — in the terms of the law of Wurtz — it may be regarded as having lost.

The constructive power of multivalent atoms is shown in many reactions in which they serve to bind together two or more molecules into one, thus: —

$$2\ \underset{\text{Acetic Acid.}}{H\text{-}O\text{-}C_2H_3O} + \underset{\text{Zinc.}}{\overset{II}{Zn}} = \underset{\text{Zincic Acetate}}{Zn{=}O_2{=}(C_2H_3O)_2} + H_2$$

and

$$\underset{\text{Aluminum.}}{\overset{VI}{[Al_2]}} + 6\ \underset{\text{Sodic Hydrate}}{Na\text{-}O\text{-}H} = \underset{\text{Sodic Aluminate.}}{(Na\text{-}O)_6{=}[Al_2]} + 3\ H_2.$$

On the other hand, when in a reaction such a multivalent

* See "The New Chemistry," Chapter XII.

atom is removed, the molecule breaks apart. Phosphoric chloride, for example, which tends to exchange two atoms of chlorine for one of oxygen, has a remarkable power of this sort.

$$\underset{\text{Acetic Acid.}}{H\text{-}O\text{-}C_2H_3O} + PCl_5 = PCl_3O + H\text{-}Cl + \underset{\text{Acetylic Chloride.}}{C_2H_3O\text{-}Cl}.$$

In the second place, it is obvious that multivalent atoms by combining with each other may give rise to nuclei around which molecules of very great complexity can be constructed. Examples of this have already been given in the symbols of valerianic acid on page 93, where the atoms of carbon, locked together like so many vertebræ, form the framework to which the other atoms are fastened, and thus a complex molecular structure is rendered in a wonderful measure compact and stable. There is a great difference in the power of multivalent atoms to unite with each other. As a general rule, even dissimilar atoms of high quantivalence will not combine, and, except in the case of carbon, the union between similar atoms is limited to a very small number of individuals. Carbon is unique in this respect. Its atoms appear to have an unlimited power of combination with each other, and for this reason the compounds of carbon already known exceed those of all the other elements combined.

Since the carbon atoms are quadrivalent, it follows that, when chained together by the smallest possible number of bonds, the atom-fixing power of the nuclei thus formed is always equal to twice the number of carbon atoms plus two $(2n + 2)$. Thus,

$$CH_4 \quad C_2H_6 \quad C_3H_8 \quad C_4H_{10} \quad C_5H_{12} \text{ etc.}$$

are the symbols of well-known hydrocarbons called paraffines, and

$$\underset{\text{Methyl.}}{CH_3} \quad \underset{\text{Ethyl.}}{C_2H_5} \quad \underset{\text{Propyl.}}{C_3H_7} \quad \underset{\text{Butyl.}}{C_4H_9} \quad \underset{\text{Amyl.}}{C_5H_{11}} \text{ etc.}$$

are the symbols of univalent radicals. These last are characteristic constituents of an important class of compounds called alcohols, and hence they are usually called the alcohol radicals. If in these atomic groups we substitute an atom of oxygen for two atoms of hydrogen, we obtain

CHO C_2H_3O C_3H_5O C_4H_7O C_5H_9O etc.,
Formyl. Acetyl. Propionyl. Butyryl. Valeryl.

also univalent radicals, which enter into the composition of an important class of acids to which we have already referred.

If, however, a definite number of carbon atoms, forming the nucleus of a molecule, are united by more than the smallest possible number of bonds, then it is obvious that the atom-fixing power of such a nucleus must fall off two units for every pair of bonds employed in holding the carbon atoms together. Thus, parallel to the paraffines mentioned above, we have another series of hydrocarbons called olefines, whose symbols are

C_2H_4 C_3H_6 C_4H_8 C_5H_{10} etc.
Ethylene. Propylene. Butylene. Amylene.

We may either conceive of the carbon atoms which form the nuclei of these molecules as arranged in an open chain with two of the atoms united by a double link, or we may conceive of them as arranged in a closed chain in which every atom will stand in the same relation to its neighbors. For example, for C_3H_6 either

or

Moreover, the chains may be forked, as in the symbols of the isomeric forms of valerianic acid already given, and in any case the precise structure is a question for investigation;* but whatever that structure may be, there is one link in the chain not essential to preserve the integrity of the molecule, and we should naturally suppose that this could be easily broken, and two additional univalent atoms, or their equivalents, united to the nucleus at the two bonds thus opened. Hence we are not surprised to find that the olefines are bivalent radicals, and will unite directly with Cl_2 or Br_2 to form such compounds as

$C_2H_4Br_2$ $C_3H_6Br_2$ $C_4H_8Cl_2$ $C_5H_{10}Cl_2$

* If the student will represent the carbon skeletons of the graphic symbols on page 93 in the same way that we have represented that of propylene above (second form), he will see what is meant by a forked chain. If next he unites the first two carbon atoms of the main chain by a double or treble bond and diminishes the number of open bonds to correspond, the whole theory of what we are here discussing will become more plain.

A further illustration of the same principle may be found in a remarkable hydrocarbon gas called acetylene, which is a frequent product of imperfect combustion, and may be formed by the direct union of its elements. The symbol of acetylene is C_2H_2, and it acts both as a dyad and as a tetrad radical, forming with bromine two compounds, $C_2H_2Br_2$ and $C_2H_2Br_4$. Still more remarkable is the structure of the well-known hydrocarbon benzol, whose symbol is C_6H_6. The chemical relations of this compound and its numberless derivatives are well explained by the theory of Kekulé, that its nucleus consists of a closed chain of six carbon atoms united alternately by single and double links, so that each of the atoms has one bond free to combine with atoms of hydrogen or their equivalents. Indeed, some chemists have thought the structure of this nucleus so thoroughly determined, that they have numbered the atoms of carbon, and in many cases the reactions of the benzol derivatives seem to indicate the relative points of the chain at which the various radicals are attached. This theory, however, has been questioned, and other schemes of arranging the atoms have been proposed as better explaining the facts. But it would be wholly premature to discuss such questions at present, and our object has been gained if we have given the student a conception of the general principles involved.

It will be seen from the above illustrations that the quantivalence of a group of similar atoms must depend on the number of links by which they are united to each other, and may therefore vary very greatly. The same phenomenon is presented by other elements, although not nearly to the same extent as with carbon. Thus not unfrequently a group of two atoms of a bivalent element has the same quantivalence as a single atom. For example, there are two compounds of mercury and chlorine, $Hg\text{-}Cl_2$ and $[Hg_2]''Cl_2$ or $Cl\text{-}Hg\text{-}Hg\text{-}Cl$. So also we have $Cu\text{-}O$ and $[Cu_2]''O$. We also find another illustration of the same principle in an important class of tetrad elements whose atoms readily pair together, forming an atomic group which is sextivalent. Thus are formed the well-known compounds

$$[Al_2]^{\equiv}Cl_6 \qquad [Fe_2]^{\equiv}O_3 \qquad [Cr_2]^{\equiv}O_3 \text{ etc.}$$

When these same elements enter into combination by single atoms, they are almost invariably bivalent, and thus we have, in several cases, two very distinct classes of compounds, the one formed with the single and the other with the double atom of the element; for example,

$$Mn{=}Cl_2 \text{ and } [Mn_2]{\equiv}Cl_6 \qquad Fe{=}O \text{ and } [Fe_2]{\equiv}O_3$$

It will be noticed that, although in the compounds of the second class the quantivalence of the single atoms is twice as great as it is in the first, yet their atom-fixing power is only increased by one half, and hence the name of *sesqui*-oxides or *sesqui*-chlorides, etc., which is frequently applied to them.

In order to distinguish the groups of similar atoms whose affinities are all open, from those groups where the affinities are in part closed by the union of the atoms among themselves, we may, as just shown, enclose the symbols of the last in brackets; and this rule will generally be followed. In most cases, however, the relations of the parts of the symbol are sufficiently evident without this aid.

QUESTIONS AND PROBLEMS.

1. What bearing have the phenomena of substitution on the doctrine of the structure of molecules? Does the circumstance that the properties of the substitution products are frequently quite different from those of the original substance invalidate the doctrine?

2. How does the action of chlorine on acetic acid indicate that the molecules of this compound have a definite structure? On what particular fact does this evidence chiefly rest?

3. What bearing have the phenomena of isomorphism on the question of the structure of molecules? Enforce the argument by some familiar illustrations.

4. State the argument on which is based the assumption that in the molecules of marsh gas there are four masses of hydrogen united to a single mass of carbon, but otherwise independent of each other.

5. How do you explain the fact, that the different degrees of quantivalence of the same element are, as a rule, either all even or all odd?

6. Assuming that chemical attraction is a polar force, and that the poles of a given multivalent atom are normally all of equal strength, why should you expect that chlorine and hydrogen atoms, for example, would not be held by such a nucleus with the same force?

7. Give the steps of the reasoning by which the structure of methylic alcohol is established.

8. Analyze the following reactions, and show that, by comparing the reactions in each group, the structure of the various compounds may be inferred.

$$\underset{\text{Chlorine Gas.}}{Cl\text{-}Cl} + \underset{\text{Hydrogen Gas.}}{H\text{-}H} = \underset{\text{Hydrochloric Acid.}}{HCl} + \underset{\text{Hydrochloric Acid.}}{HCl}$$

$$Cl\text{-}Cl + \underset{\text{Oil of Bitter Almonds.}}{(C_7H_5O)\text{-}H} = \underset{\text{Benzoyl Chloride.}}{(C_7H_5O)\text{-}Cl} + HCl$$

$$H\text{-}Cl + \underset{\text{Potassic Hydrate.}}{K\text{-}O\text{-}H} = \underset{\text{Potassic Chloride.}}{KCl} + \underset{\text{Water.}}{H\text{-}O\text{-}H}$$

$$H\text{-}Cl + \underset{\text{Alcohol.}}{(C_2H_5)\text{-}O\text{-}H} = \underset{\text{Ethylic Chloride.}}{(C_2H_5)\text{-}Cl} + H\text{-}O\text{-}H$$

$$\underset{\text{Sulphohydric Acid.}}{H,H\text{-}S} + \underset{\text{Phosphoric Chloride.}}{P\equiv Cl_5} = PO\equiv Cl_3,S + HCl + HCl$$

$$\underset{\text{Thiacetic Acid.}}{H,(C_2H_3O)\text{-}S} + P\equiv Cl_5 = P\equiv Cl_3,S + \underset{\text{Acetylic Chloride.}}{(C_2H_3O)\text{-}Cl} + HCl$$

$$\underset{\text{Potassic Hydrate.}}{K_2\text{-}O_2\text{-}H_2} + \underset{\text{Cyanic Acid.}}{(CO),H\text{-}N} = \underset{\text{Potassic Carbonate.}}{K_2\text{-}O_2\text{-}(CO)} + \underset{\text{Ammonia.}}{H,H,H\text{-}N}$$

$$K_2\text{-}O_2\text{-}H_2 + \underset{\text{Cyanic Ether.}}{(CO),(C_2H_5)\text{-}N} = K_2\text{-}O_2\text{-}(CO) + \underset{\text{Ethylamine.}}{H,H,(C_2H_5)\text{-}N}$$

9. Represent in a graphic form the structure of the following molecules whose symbols are given above, — ethylamine, cyanic acid, cyanic ether, thiacetic acid.

10. Why is it that the successive additions of CH_2 in the series of alcohols do not change the atomicity of the alcohol radicals?

11. In what different ways may the symbol of propylene be represented graphically? Exhibit in the same way the structure of acetylene and benzol.

12. Represent by graphic symbols the structure of the following derivatives from benzol, and containing the same nucleus: —

Aniline,	$H, H, C_6H_5\text{-}N$
Benzoic Acid,	$(C_6H_5\text{-}CO)\text{-}O\text{-}H$
Benzamide,	$H, H, (C_6H_5\text{-}CO)\text{-}N$

13. The radical allyl C_3H_5 is univalent in oil of garlic, $(C_3H_5)_2\text{=}S$, and in allylic alcohol, $(C_3H_5)\text{-}O\text{-}H$, but trivalent in glycerine, $(C_3H_5)\text{≡}O_3\text{=}H_3$. Moreover, this radical when set free doubles, forming a volatile hydrocarbon oil, which has the composition $(C_3H_5)\text{=}(C_3H_5)$, and which combines directly with bromine, the resulting product having the symbol $(C_3H_5)\text{-}(C_3H_5)\text{≡}Br_4$. Represent these symbols by the graphic method, and thus explain the different relations of the radical.

14. Represent by the graphic method the symbols of potassic carbonate, $K_2\text{=}O_2\text{=}(CO)$, and potassic oxalate, $K_2\text{=}O_2\text{=}(C_2O_2)$, and show that each forms a perfect molecular unit.

15. Represent by the graphic method the following symbols. Consider in each case if more than one way is possible.

C_2H_4 Ethylene. $\quad H_2\text{=}O_2\text{=}C_2H_4$ Glycol. $\quad H_2\text{=}O_2\text{=}C_2H_2O$ Glycollic Acid.

$H, H_2\text{=}N\text{-}(C_2H_2O)\text{-}O\text{-}H$ Glycocol. $\quad H, (C_6H_5\text{-}CO)\text{=}N\text{-}(C_2H_2O)\text{-}O\text{-}H$ Hippuric Acid.

$H_2\text{=}O_2\text{=}(C_3H_6)$ Propyl Glycol. $\quad H_2\text{=}O_2\text{=}(C_3H_4O)$ Lactic Acid.

16. What is the quantivalence of Al in the symbol $[Al\text{-}Al]Cl_6$? Is there any difference in the quantivalence of Fe in the two compounds $Fe\text{=}O_2\text{=}CO$ and $[Fe\text{-}Fe]\text{≡}O_6\text{≡}(SO_2)_3$? Answer the questions by the aid of graphic symbols.

17. Is there any difference in the quantivalence of nitrogen in potassic nitrite, $K\text{-}O\text{-}NO$, and potassic nitrate, $K\text{-}O\text{-}NO_2$? In what two ways may the last symbol be represented graphically?

18. The symbol $[Cu_2]Cl_2$ represents a single molecule, while Na_2Cl_2 represents two molecules, and would be more properly written $2\,NaCl$. What is the difference in the two cases, and on what evidence do these symbols rest? Is there the same proof of the correctness of $[Hg_2]Cl_2$? See Table III.

CHAPTER IX.*

BASES, ACIDS, AND SALTS.

36. **Hydrates, Alkalies, Bases.** — It is not unfrequently the case that the technical terms of a science remain in use long after they have lost their original meaning. This is peculiarly true of those which we have placed at the head of this section. They have, with the exception of the first, come down to us from the period of alchemy, and are still retained in the language of trade and in many works on practical science, with a peculiar meaning which they have acquired during the last hundred years under the teaching of the dualistic theory. Since they, in many cases at least, suggest erroneous conceptions in regard to the constitution of chemical compounds, it would be well if they could be discarded altogether; but as this is impracticable, we must endeavor to give to them as definite a meaning as possible.

The term *hydrate* is applied to a class of compounds which were formerly supposed to contain water as such, but which are now believed to have no closer relation to water than is indicated by the circumstance that they have the same type of structure, and may be formed from water by replacing half of its hydrogen with some metallic atom or compound radical acting like a metallic atom. Thus, by acting on water with potassium, we obtain potassic hydrate; or, if we use sodium, we obtain sodic hydrate.

$$\underset{\text{Water.}}{2\,H\text{-}O\text{-}H} + \underset{\text{Potassium.}}{K\text{-}K} = \underset{\text{Potassic Hydrate.}}{2\,K\text{-}O\text{-}H} + \underset{\text{Hydrogen Gas.}}{H\text{-}H}$$

$$\underset{\text{Water.}}{2\,H\text{-}O\text{-}H} + \underset{\text{Sodium.}}{Na\text{-}Na} = \underset{\text{Sodic Hydrate.}}{2\,Na\text{-}O\text{-}H} + \underset{\text{Hydrogen Gas.}}{H\text{-}H} \qquad [38]$$

* In studying this chapter the student should endeavor to remember the names and symbols of the different compounds mentioned. Hitherto we have been chiefly employed with the forms of the symbols, and this exercise of the memory has not been expected.

Both of these hydrates, and also those of the very rare but closely allied metals, lithium, cæsium, and rubidium, are very soluble in water, and yield solutions which corrode the skin and convert the fats into soaps. All the substances possessing these caustic qualities which were known to the alchemists were called by them *alkalies*, and this term is now applied to the five hydrates just enumerated, as well as to ammonia (see below). The first two of these are commercial products, and have important applications in the arts. They all differ from the hydrates of other metals in that they cannot be decomposed by heat alone.

Again, if we act on water with calcium or magnesium, we obtain calcic or magnesic hydrate; but the double molecule of water is then decomposed by these bivalent metals to form a single molecule of the hydrate.

$$\underset{\text{Water.}}{H_2{=}O_2{=}H_2} + \overset{\text{II}}{\underset{\text{Calcium.}}{Ca}} = \underset{\text{Calcic Hydrate.}}{Ca{=}O_2{=}H_2} + \underset{\text{Hydrogen Gas.}}{H{-}H} \qquad [39]$$

$$\underset{\text{Water.}}{H_2{=}O_2{=}H_2} + \overset{\text{II}}{\underset{\text{Magnesium.}}{Mg}} = \underset{\text{Magnesic Hydrate.}}{Mg{=}O_2{=}H_2} + \underset{\text{Hydrogen Gas.}}{H{-}H}$$

These two hydrates, as well as those of the allied metals, barium and strontium, although much less soluble in water than the alkalies, still dissolve in this common solvent to a limited extent, and manifest decided caustic qualities. When dry they have an earthy appearance, and hence are frequently known as the alkaline earths. They also differ from the true alkalies in the fact that they are readily decomposed by heat; and since they are then resolved into water and a metallic oxide, as the following reaction shows, the opinion formerly entertained in regard to their composition was not unnatural.

$$\underset{\text{When heated.}}{Mg{=}O_2{=}H_2} = MgO + H_2O \qquad [40]$$

Moreover, when the anhydrous oxides are mixed with water, they enter into direct union with a portion of the liquid. This combination is usually attended with the evolution of great heat, and the process is known as slaking.

$$CaO + H_2O = Ca{=}O_2{=}H_2. \qquad [41]$$

There are many other metallic hydrates which are still more readily decomposed by heat. These, as a rule, cannot be formed by the direct union of the corresponding metallic oxide and water, but may be obtained by adding to a solution of a salt of the metal one of the soluble hydrates mentioned above. Thus: —

$$(\underset{\text{Cupric Chloride.}}{Cu''Cl_2} + 2\,Na'\text{-}O\text{-}H + Aq) = (\underset{\text{Cupric Hydrate.}}{Cu''O_2''H_2} + 2\,\underset{\text{Sodic Chloride.}}{Na'Cl} + Aq)$$

[42]

$$(\underset{\text{Zincic Chloride.}}{Zn''Cl_2} + 2\,K'\text{-}O\text{-}H + Aq) = (\underset{\text{Zincic Hydrate.}}{Zn''O_2''H_2} + 2\,\underset{\text{Potassic Chloride.}}{K'Cl} + Aq)$$

$$([\underset{\text{Ferric Chloride.}}{Fe_2'''}]Cl_6 + 3\,Ba''O_2''H_2 + Aq) = ([Fe_2'''\equiv O_6''\equiv H_6] + 3\,\underset{\text{Baric Chloride.}}{Ba''Cl_2} + Aq)$$

The hydrates may be regarded as compounds of the metallic atoms with the compound radical hydroxyl, and their symbols written thus: —

$$\underset{\text{Calcic Hydrate.}}{Ca''(\overset{\text{I}}{HO})_2} \qquad \underset{\text{Ferrous Hydrate.}}{Fe''(\overset{\text{I}}{HO})_2} \qquad \underset{\text{Chromic Hydrate.}}{[\overset{\text{VI}}{Cr_2}]'''(\overset{\text{I}}{HO})_6}$$

Ammonic Hydrate. — Closely allied to these metallic hydrates is a very remarkable compound, formed by dissolving ammonia gas, NH_3, in water. Although the product resembles, in many of its physical relations, a simple solution of gas in water, yet the compound in all its chemical relations acts like a metallic hydrate,

$$\underset{\text{Ammonia Gas.}}{NH_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonic Hydrate.}}{\overset{\text{I}}{NH_4}\text{-}O\text{-}H}$$

which has led chemists to write its symbol after the type of water, and to assume the existence of a univalent compound radical $\overset{\text{I}}{NH_4}$, to which has been given the name of ammonium.

Metallic Oxides or Basic Anhydrides. — Closely allied to the metallic hydrates, in the relation we are now considering, are many of the simple compounds of the metals with oxygen, which are called in general metallic oxides. Such compounds as

$$\underset{\text{Argentic Oxide.}}{Ag\text{-}O\text{-}Ag} \quad \underset{\text{Calcic Oxide.}}{Ca''O} \quad \underset{\text{Baric Oxide.}}{Ba''O} \quad \underset{\text{Plumbic Oxide.}}{Pb''O} \quad \underset{\text{Ferrous Oxide.}}{Fe''O} \quad \underset{\text{Cupric Oxide.}}{Cu''O}$$

may be regarded as formed from one or more molecules of water, by replacing all the atoms of hydrogen with those of some metal; and these oxides as well as the hydrates before mentioned are frequently classed together under the common title of *bases*, although it would be best to confine this term to the metallic hydrates alone, and to distinguish the *basic oxides* as *basic anhydrides* (§ 38).

Salts. — The atoms of hydrogen still remaining in a metallic hydrate may be replaced with the atoms of a well-defined class of non-metallic elements and compound radicals; and, for a reason which will soon appear, the replacing atoms are called acid or negative radicals.*

From this replacement results a new class of compounds we call *salts*. Thus,

$K\text{-}O\text{-}H$ gives $K\text{-}O\text{-}Cl$, also $K\text{-}O\text{-}NO_2$ and $K\text{-}O\text{-}(C_2H_3O)$
Potassic Hydrate. Potassic Hypochlorite. Potassic Nitrate. Potassic Acetate.

$Ca{=}O_2{=}H_2$ gives $Ca{=}O_2{=}SO_2$ $Ca{=}O_2{=}CO$ $Ca{=}O_2{=}(C_2H_3O)_2$
Calcic Hydrate. Calcic Sulphate. Calcic Carbonate. Calcic Acetate.

37. **Acids.** — Opposed in chemical properties to the so-called bases is another very important class of compounds called *acids*. They derive their name from the fact that they are generally soluble in water and have a sharp or sour taste, although there are many exceptions to the rule. Like the bases, they all contain hydrogen; this hydrogen, however, can no longer be replaced

* The word *radical*, as used in chemistry, stands for any atom or group of atoms which is, *for the moment*, regarded as a chief constituent of the molecules of a given compound, and which does not lose its integrity in the ordinary chemical reactions to which the substance is liable. The distinction between basic and acid radicals (or positive and negative radicals, as they are more frequently called) will become clear as we advance. It is sufficient for the present to state that, although these terms imply an *opposition of relations* rather than a difference of qualities, yet, as a general rule, the metallic atoms are basic radicals, while the non-metallic atoms are acid radicals. It may be added, that among compound radicals those consisting of carbon and hydrogen alone are usually basic, and those containing also oxygen usually acid; and further, that, of the two most important radicals containing nitrogen, ammonium (NH_4) is strongly basic, and cyanogen (CN) as decidedly acid. In this book, with few exceptions, the basic radicals are always placed on the left-hand, and the acid radicals on the right-hand side of the molecular symbols.

by non-metallic elements or negative radicals, but only by metallic elements and positive radicals, and it is herein that the chief distinction lies. Moreover, the opposition of these two classes of compounds also appears in the fact that, while in bases the replaceable hydrogen atoms are united to a metallic atom or positive radical, which for this reason we frequently call a basic radical, in the acids, on the other hand, these same hydrogen atoms are united as a rule to a non-metallic atom or negative radical, frequently also called, as above, an acid radical. In most cases there is a vinculum which unites the two parts of the molecule; and both in acids and in bases this vinculum consists usually of one or more oxygen atoms, although in a large class of acids the hydrogen atoms are united directly to the radical without any such connection. The acids of this class have by far the simplest constitution; and we will give examples of these first, adding in each case a reaction to illustrate the acid relations of the compound. In studying these reactions, it must be borne in mind that the evidence of acidity is in each case to be found in the fact that one or more of the hydrogen atoms of the compound may be replaced by positive radicals or metallic atoms. This replacement may be obtained in one of four ways, — by acting on the acid, either with the metal itself, or with a metallic oxide, or with a metallic base, or with a metallic salt.

$$\underset{\text{Hydrochloric Acid.}}{(2\,HCl + Aq)} + \underset{\text{Sodium.}}{Na\text{-}Na} = \underset{\text{Sodic Chloride.}}{(2\,NaCl + Aq)} + \boxed{H}\text{-}\boxed{H}$$

$$\underset{\text{Zincic Oxide.}}{(2\,HCl + Aq) + ZnO} = \underset{\text{Zincic Chloride.}}{(ZnCl_2 + H_2O + Aq)}$$

$$\underset{\text{Hydrobromic Acid.}}{(HBr} + \underset{\text{Potassic Hydrate.}}{K\text{-}O\text{-}H + Aq)} = \underset{\text{Potassic Bromide.}}{(KBr + H_2O + Aq)} \qquad [43]$$

$$\underset{\text{Hydriodic Acid.}}{(HI} + \underset{\text{Argentic Nitrate.}}{Ag\text{-}O\text{-}NO_2 + Aq)} = \underset{\text{Argentic Iodide.}}{(AgI} + \underset{\text{Nitric Acid.}}{(H\text{-}O\text{-}NO_2 + Aq)}$$

We will next give examples of more complex acids, in which the two parts of the molecule are united by a vinculum of oxygen atoms.

$$\underset{\text{Acetic Acid.}}{(H\text{-}O\text{-}(C_2H_3O)} + \underset{\text{Sodic Hydrate.}}{Na\text{-}O\text{-}H + Aq)} = \underset{\text{Sodic Acetate.}}{(Na\text{-}O\text{-}(C_2H_3O)} + H_2O + Aq)$$

$$\underset{\text{Sulphuric Acid.}}{(H_2{=}O_2{=}SO_2 + Aq)} + \underset{\text{Cupric Oxide.}}{CuO} = \underset{\text{Cupric Sulphate.}}{(Cu{=}O_2{=}SO_2 + H_2O + Aq)}$$

$$\underset{\text{Phosphoric Acid.}}{(H_3{\equiv}O_3{\equiv}PO} + \underset{\text{Potassic Hydrate.}}{3\,K\text{-}O\text{-}H} + Aq) = \underset{\text{Potassic Phosphate.}}{(K_3{\equiv}O_3{\equiv}PO} + 3\,H_2O + Aq)$$

Such acids as these are called oxygen acids. Like the hydrates, they may be regarded as compounds of hydroxyl, but with negative instead of positive radicals, thus: —

$$\underset{\text{Nitric Acid.}}{HO\text{-}NO_2} \qquad \underset{\text{Sulphuric Acid.}}{(HO)_2{=}SO_2} \qquad \underset{\text{Phosphoric Acid.}}{(HO)_3{\equiv}PO.}$$

This mode of writing the symbols is not only frequently convenient, but has been of real value by bringing out unexpected and important relations. It does not, however, indicate any fundamental difference of opinion in regard to the constitution of these hydrates, and this at once appears when the symbols are put into the graphic form.

When an acid, like acetic acid, contains but one atom of hydrogen, which is replaceable by a metallic atom or a positive radical, it is called monobasic; when, like sulphuric acid, it contains two such hydrogen atoms, it is called dibasic; when, like phosphoric acid, it contains three, it is tribasic, etc. Moreover, one evidence of this difference of basicity is found in the fact, that, whereas a monobasic acid can only form one salt with a univalent radical, a dibasic acid can form two, and a tribasic three. Thus, while we have only one sodic nitrate, there are two sodic sulphates and three sodic phosphates.

$$\underset{\text{Sodic Nitrate.}}{Na\text{-}O\text{-}NO_2} \qquad \underset{\text{Acid Sodic Phosphate, or Dihydro-sodic Phosphate.}}{H_2Na{\equiv}O_3{\equiv}PO}$$

$$\underset{\text{Acid Sodic Sulphate.}}{H,Na{=}O_2{=}SO_2} \qquad \underset{\text{Neutral Sodic Phosphate, or Hydro-disodic Phosphate.}}{HNa_2{\equiv}O_3{\equiv}PO} \qquad [44]$$

$$\underset{\text{Neutral Sodic Sulphate.}}{Na_2{=}O_2{=}SO_2} \qquad \underset{\text{Basic Sodic Phosphate, or Trisodic Phosphate.}}{Na_3{\equiv}O_3{\equiv}PO}$$

There is, however, but one calcic sulphate; for, since the calcium atoms are bivalent, a single one is sufficient to replace both of the hydrogen atoms in the acid.

38. **Acid Anhydrides.** — Besides the acids properly so called, all of which contain hydrogen, there is another class of com-

pounds which bear the same relation to the true acids which the metallic oxides bear to the true bases. To avoid confusion, compounds of this class have been distinguished as *anhydrides*,* and they may be regarded as one or more molecules of water in which all the hydrogen has been replaced by negative or acid radicals. As among the most important of these we may enumerate Sulphuric Oxide, $SO_2{=}O$ or SO_3, Nitric Pentoxide, $NO_2{-}O{-}NO_2$ or N_2O_5, Carbonic Dioxide, CO_2, Phosphoric Oxide, P_2O_5, and Silicic Oxide, $\overset{IV}{Si}O_2$. Most of the anhydrides unite directly with water to form acids, and several of the acids, when heated, give off water and pass into anhydrides. [Compare 40 and 41.]

$$H_2O + SO_3 = H_2{=}O_2{=}SO_2$$

$$3H_2O + P_2O_5 = 2H_3{=}O_3{=}PO \qquad [45]$$

$$\underset{\text{Silicic Acid.}}{H_4{=}O_4{=}Si} = \underset{\text{Silicic Anhydride.}}{SiO_2} + 2H_2O$$

$$\underset{\text{Boric Acid.}}{2H_3{=}O_3{=}B} = \underset{\text{Boric Anhydride.}}{B_2O_3} + 3H_2O$$

Moreover, in many cases these anhydrides will combine directly with the metallic oxides to form salts. Thus, baric oxide burns in the vapor of sulphuric anhydride, yielding baric sulphate; and lime also unites directly with the same anhydride, although with less energy, forming calcic sulphate.

$$BaO + SO_3 = BaO, SO_3 \quad \text{and} \quad CaO + SO_3 = CaO, SO_3$$

We are thus led to the old formulæ of the dualistic system, according to which the metallic oxides were the only true bases, the anhydrides were the only true acids, and the two were regarded as paired in all true salts. But although in its modern theories our science has fortunately left the ruts to which the dualistic ideas for so long limited its progress, yet it must be remembered that, according to our present definitions, these dualistic formulæ are perfectly legitimate, and still give the simplest exposition of a large number of important facts.

* More precisely *acid anhydrides;* but as the basic anhydrides are usually called simply metallic oxides, the qualifying term is seldom added.

39. **Salts.**—The definition of the term *salt* has been clearly implied in the definitions of *base* and *acid* already given. It is any acid in which one or more atoms of hydrogen have been replaced with metallic atoms or basic radicals; it is any base in which the hydrogen atoms have been more or less replaced by non-metallic atoms or acid radicals; or it may be the product of the direct union of a metallic oxide and an anhydride. A neutral salt is, properly speaking, one in which all the hydrogen atoms, whether of base or acid, have been replaced as just stated. A basic salt is one in which one or more of the hydrogen atoms of the base remain undisturbed, and therefore still capable of replacement by acid radicals. An acid salt is one in which one or more of the hydrogen atoms of the acid remain undisturbed, and therefore capable of replacement by basic radicals.

But besides the basic and acid salts which come under these definitions, there are also others which can be most simply defined as consisting of several molecules of the metallic oxide to one of anhydride, or of several molecules of anhydride to one of the metallic oxide.

As an example of acid salts of the second class we have, besides the two sodic sulphates mentioned on page 108, also a third, which may be written $Na_2O, 2SO_3$. This is easily obtained by simply heating the acid sulphate.

$$\underset{\text{Acid Sodic Sulphate.}}{2\,(H, Na\text{-}O_2\text{-}SO_2)} = \underset{\text{Sodic Bisulphate.}}{Na_2O, 2\,SO_3} + \underset{\text{Water.}}{H_2O} \qquad [46]$$

If heated to a still higher temperature, one molecule of the anhydride is set free, and the salt falls back into the neutral sulphate.

$$\underset{\text{Bisulphate.}}{Na_2O, 2\,SO_3} = \underset{\text{Neutral Sulphate.}}{Na_2O, SO_3} + \underset{\text{Anhydride.}}{SO_3}$$

This reaction justifies the dualistic form given to the symbol; but other relations of the bisulphate may be better expressed by the following typical formula,—

$$\underset{\text{Sodic Bisulphate.}}{Na_2\text{-}O_2\text{-}(\overset{\text{II}}{SO_2}\text{-}O\text{-}SO_2)} = \underset{\text{Neutral Sulphate.}}{Na_2\text{-}O_2\text{-}SO_2} + \underset{\text{Anhydride.}}{SO_3}$$

in which a group of two atoms of SO_2, soldered together by one atom of oxygen, acts as a bivalent radical.

As an example of a basic salt of the second class we have, in addition to the two plumbic acetates of the normal type,

$$\underset{\text{Neutral Plumbic Acetate.}}{Pb{=}O_2{=}(C_2H_3O)_2} \quad \text{and} \quad \underset{\text{Basic Plumbic Acetate.}}{Pb{=}O_2{=}(C_2H_3O)_2,H}$$

a third salt containing three times as much lead, —

$$\underset{\text{Triplumbic Acetate.}}{(Pb{-}\overset{\text{II}}{O}{-}Pb{-}O{-}Pb){=}O_2{=}(C_2H_3O)_2} \qquad [47]$$

in which a group of three atoms of lead, soldered together by two atoms of oxygen, acts as a bivalent radical. It is evident that theoretically any number of multivalent radicals might be united in this way, and also that the complex radical thus formed will have a quantivalence easily determined by estimating the number of bonds which remain unsatisfied; but practically the grouping cannot be carried to a very great extent, for the stability of the radical diminishes with its complexity, and a condition is soon reached when it can no longer sustain, if we may so express it, its own weight. Moreover, while some radicals, like the atoms of lead, copper, mercury, and iron, are prone to group themselves in this way, the larger number show but little tendency to this mode of union.

The symbols of these acetates may also be written on the dualistic type, which represents them as compounds of plumbic oxide, PbO, and acetic anhydride, $C_4H_6O_3$. We have, then,

$$\underset{\text{Neutral Plumbic Acetate.}}{PbO,\,C_4H_6O_3} \quad \text{and} \quad \underset{\text{Triplumbic Acetate.}}{3\,PbO,\,C_4H_6O_3} \qquad [48]$$

and we may thus best illustrate the important fact that the second compound is prepared by combining with the first an additional quantity of plumbic oxide.

It will appear, on reviewing the symbols of the acids, bases, and salts given in this section, that in by far the greater number the two parts of the molecule are held together by one or more atoms of oxygen, which act as a vinculum. Such compounds are called oxygen salts, using the word *salt*, as is fre-

quently done, to stand for acids and bases, as well as for the true metallic salts; and in fact they all belong to the same type of chemical compounds. Since oxygen plays so important a part in terrestrial nature, we might well expect that these oxygen compounds would hold a very conspicuous place in our chemical science; and such is indeed the fact. During the dualistic period the study of chemistry was almost wholly confined to the oxygen compounds, and even now they occupy by far the largest share of a chemist's attention.

There is, however, another element, namely, sulphur, which is capable of filling the place occupied by oxygen in many of its compounds, and thus may be formed a distinct class of bodies which are called sulphur salts. These compounds are not nearly so numerous as the oxygen salts, and have not been so well studied, so that a few examples will be sufficient to illustrate their general composition, and the relations which they bear to the corresponding oxygen compounds.

Oxygen Salts.	*Sulphur Salts.*
$H\text{-}O\text{-}H$	$H\text{-}S\text{-}H$
Water or Hydric Acid.	Sulphohydric Acid.
$K\text{-}O\text{-}H$	$K\text{-}S\text{-}H$
Potassic Hydrate.	Potassic Sulphohydrate
$K_2{}^{\cdot}O_2{}^{\cdot}CO$	$K_2{}^{\cdot}S_2{}^{\cdot}CS$
Potassic Carbonate.	Potassic Sulphocarbonate.

40. **Test-Papers.** — The soluble bases and acids, when dissolved in water, cause a striking change of color in certain vegetable dyes, and these characteristic reactions give to the chemist a ready means of distinguishing between these two important classes of compounds. The two dyes chiefly used for this purpose are turmeric and litmus, and strips of paper colored with the dyes are employed in testing. Turmeric paper, which is naturally yellow, is turned brownish red by bases, while litmus paper, which is naturally blue, is turned red by acids, and in both cases the natural color is restored by a compound of the opposite class.

If to a solution of a strong base, like sodic hydrate, we add slowly and carefully a solution of a strong acid, like sulphuric,

we shall at last reach a condition in which the solution affects neither test-paper, and it is then said to be *neutral*. On evaporating this solution we obtain a neutral salt, like sodic sulphate, and the presence in the solution of the slightest excess of acid or base beyond the amount required to form this salt would have been made evident by the test-papers. In such cases, we may therefore use these test-papers to distinguish between acid, basic, and neutral salts, but only with great caution; for we find that when, as in acid sodic carbonate, a strong base is associated with a weak acid, the reaction is still basic, although the acid may be greatly in excess, and, on the other hand, when, as in cupric sulphate, a weak base has been associated with a strong acid, the reaction may be strongly acid even in the basic salts. The explanation of these apparent anomalies is to be found in the fact that these colored reagents are all salts themselves, and the reactions examples of metathesis. The coloring matter of these dyes is an acid which varies its tint according as the hydrogen atoms have or have not been replaced; and when, for any reason, the acid or base of the salt examined is not in a condition to determine the necessary metathesis, the characteristic change of color does not take place.

Unfortunately, the facts just stated have led to great confusion in the use of the words *acid* and *basic* as applied to salts, since these terms sometimes have reference solely to the number of atoms of hydrogen, in the acid or base, which have not been replaced in the formation of the salt, and at other times refer to the reactions of the salt on the colored reagents just described. A confusion of this sort must have been noticed in the first and commonly used names of the three phosphates of soda on page 108. The so-called neutral phosphate is theoretically an acid salt, and the basic phosphate a neutral salt, but the salts give with test-papers the reactions which their names indicate. The theoretical is the only legitimate use, and the one we shall adhere to in this book, except in regard to names of compounds which cannot be arbitrarily changed.

41. **Alcohols, Fat Acids, Ethers.** — The hydrocarbon radicals mentioned in § 35 yield a very large number of compounds

which are closely allied to the hydrates and anhydrides, both acid and basic, just described. If one of the hydrogen atoms in the molecule of water is replaced by either of the univalent basic radicals, methyl, ethyl, propyl, etc., we obtain a class of compounds, already referred to, called alcohols, of which our common alcohol is the most important. On the other hand, if the atom of hydrogen is replaced by one of the univalent acid radicals, formyl, acetyl, propionyl, etc., we obtain the parallel class of acid compounds, of which acetic acid (vinegar) is the best known, but which also includes a large number of fatty substances closely related to our ordinary fats. Hence the name Fat Acids, by which this class of compounds is generally designated.

Basic Hydrates, or Alcohols.

Methylic Alcohol (wood spirits),	CH_3-O-H
Ethylic Alcohol (common alcohol),	C_2H_5-O-H
Propylic Alcohol,	C_3H_7-O-H
Butylic Alcohol,	C_4H_9-O-H
Amylic Alcohol (fusel oil),	C_5H_{11}-O-H

Acid Hydrates, or Fat Acids.

Formic Acid,	H-O-CHO
Acetic Acid,	H-O-C_2H_3O
Propionic Acid,	H-O-C_3H_5O
Butyric Acid,	H-O-C_4H_7O
Valerianic Acid,	H-O-C_5H_9O

If now we replace both of the hydrogen atoms of water by the same basic radicals mentioned above, we obtain a class of compounds called ethers, which correspond to the metallic oxides or basic anhydrides; and if we replace the two hydrogen atoms by the corresponding acid radicals, we obtain a similar series of acid anhydrides. Lastly, if we replace one of the hydrogen atoms by a basic radical, and the other by an acid radical, we get a class of compounds also called ethers (but distinguished as compound ethers), which correspond to the salts.

rides.

...rs.

$\cdot\ O\text{-}CH_3$ or $(CH_3)_2{=}O$

$H_2\text{-}O\text{-}C_2H_5$ or $(C_2H_5)_2{=}O$

...d Ethers.

$CH_3\text{-}O\text{-}C_2H_5$

$C_2H_5\text{-}O\text{-}C_5H_{11}$

... Compound Ethers.

$C_2H_5\text{-}O\text{-}C_2H_3O$

$CH_3\text{-}O\text{-}C_4H_7O$

4. Acid Anhydrides.

$C_2H_3O\text{-}O\text{-}C_2H_3O$ or $(C_2H_3O)_2{=}O$

...ydride, $C_5H_9O\text{-}O\text{-}C_5H_9O$ or $(C_5H_9O)_2{=}O$

...e radicals which the alcohols contain hold an in-...position between the strong basic radicals on the one ...the strong acid radicals on the other; and the same ...of the alcohols themselves, which hold a middle place ...the strong basic and the strong acid hydrates. This is ...ted by the following reactions; in what way it is left to ...student to inquire.

$$2\,H\text{-}O\text{-}C_2H_5 + K\text{-}K = 2\,K\text{-}O\text{-}C_2H_5 + H\text{-}H$$

$$2\,CH_3\text{-}O\text{-}H + H_2{=}O_2{=}SO_2 = (CH_3)_2{=}O_2{=}SO_2 + 2\,H_2O$$

2. **Glycols.** — If in the double molecule of water ($H_2{=}O_2{=}H_2$) replace one of the pairs of hydrogen atoms by either of the ...lent positive radicals, ethylene, propylene, butylene, etc., we ...in a series of compounds closely resembling the alcohols, ...d glycols, and by substituting the related negative radicals obtain two series of acid hydrates, which stand in the same ...tion to the glycols that the fat acids bear to the alcohols. ...se relations are shown in the following scheme, which, how-..., includes only the first five members of each of these three ...s of compounds. It should be noticed in this connection

that each of the *bivalent positive* radicals yields *two* related *negative* radicals, while the *univalent positive* radicals of the last section yield only one such negative radical; and, moreover, that the acids in the first series, although diatomic, are only monobasic, while those in the second series are both diatomic and dibasic (§ 44).

$C_2H_4{=}O_2{=}H_2$ Ethylic Glycol.	$H_2{=}O_2{=}C_2H_2O$ Glycolic Acid.	$H_2{=}O_2{=}C_2O_2$ Oxalic Acid.
$C_3H_6{=}O_2{=}H_2$ Propylic Glycol.	$H_2{=}O_2{=}C_3H_4O$ Lactic Acid.	$H_2{=}O_2{=}C_3H_2O_2$ Malonic Acid.
$C_4H_8{=}O_2{=}H_2$ Butylic Glycol.	$H_2{=}O_2{=}C_4H_6O$ Oxybutyric Acid.	$H_2{=}O_2{=}C_4H_4O_2$ Succinic Acid.
$C_5H_{10}{=}O_2{=}H_2$ Amylic Glycol.	$H_2{=}O_2{=}C_5H_8O$ Valerolactic Acid.	$H_2{=}O_2{=}C_5H_6O_2$ Pyrotartaric Acid.
$C_6H_{12}{=}O_2{=}H_2$ Hexyl Glycol.	$H_2{=}O_2{=}C_6H_{10}O$ Leucic Acid.	$H_2{=}O_2{=}C_6H_8O_2$ Adipic Acid.

Corresponding to these basic and acid hydrates we have also been able to obtain in several cases the basic and acid anhydrides, besides a very large number of compound ethers.

43. **Glycerines.** — Our common glycerine, $H_3{=}O_3{=}C_3H_5$, may be regarded as formed from three molecules of water, $H_3{=}O_3{=}H_3$, by replacing one of the groups of hydrogen atoms with the trivalent radical glyceryl (C_3H_5); and from glycerine we may derive acids, anhydrides, and ethers bearing to each other the same relations as those derived from the alcohols and glycols. The natural fats, for example, are compounds derived from glycerine and the fat acids. Glycerine is theoretically the first of a series of compounds whose successive hydrocarbon radicals differ by the well-known common difference CH_2, but only the first of the members of this series is accurately known.

44. **Atomicity and Basicity.** — We have already seen that the hydrates, both basic and acid, may be regarded as compounds of the radical hydroxyl (H-O); and this simply amounts to saying that their molecules contain one or more hydrogen atoms connected with the nucleus by an oxygen atom which serves as a vinculum. It is only the hydrogen atoms thus related to the molecule that are easily replaced by metallic atoms or other radi-

cals, and the number of such atoms determines what is called the atomicity of the compound. Thus the alcohols and fat acids are monatomic, the glycols are diatomic, and the glycerines are triatomic compounds. With the acid hydrates we sometimes distinguish between atomicity and basicity, the first being measured by the total number of hydrogen atoms that can be replaced by a simple metathetical reaction of any kind, and the last depending on the number of hydrogen atoms which can be replaced by strong basic radicals such as the metals of the alkalies. As a general rule, it is true that the basicity is the same as the atomicity, but this is not always the case. Thus lactic acid is diatomic but monobasic, and the same is true of the other acids homologous with it (page 116).

$\overset{+}{H}, \overset{-}{H}\text{-}(C_3\overset{II}{H}_4O_3)$ Lactic Acid. $\quad Na, H\text{-}(C_3\overset{II}{H}_4O_3)$ Sodic Lactate. $\quad Na, (C_7\overset{I}{H}_6O)\text{-}(C_3\overset{I}{H}_4O_3)$ Sodic Benzolactate.

$K, C_2H_5\text{-}(C_3\overset{II}{H}_4O_3)$ Potassic Ethyl-lactate. $\quad C_2H_5, C_2H_5\text{-}(C_3H_4O_3)$ Diethylic Lactate.

Only one atom of hydrogen can be replaced by a metallic radical, but a second may be replaced by either a negative or an alcoholic radical, as in the last three symbols; and in designating the atoms thus differently related to the molecular structure, it is usual to call the first basic, and the other alcoholic hydrogen.

If the symbols of lactic acid and its salts are written in the graphic form, it will be seen that, while the atomicity depends on the number of hydroxyl groups in the molecule, the basicity depends on the number of groups of the radical (*H-O-CO*) called carboxyl. This structural difference appears to be the cause of the unlike relations of the two orders of replaceable hydrogen atoms in the compounds of carbon, and it is only with these compounds that the distinction between basic and alcoholic hydrogen has been recognized.

45. **Water of Crystallization.** — Among the most striking characteristics of the class of compounds we call salts is their solubility in water, and their tendency on separating from it, in consequence of either the evaporation or the cooling of the fluid, to assume definite crystalline forms. These crystals, as a general

rule, are complex crystalline aggregates of molecules of the salt and molecules of water. The water is held in combination by a comparatively feeble force, and may be generally driven off by exposing the salt to the temperature of 100° C., when the crystals fall to powder. Sometimes it escapes at the ordinary temperature of the air, when the crystals, as before, fall to powder and are said to effloresce. It thus evidently appears that the water, although an essential part of the crystalline structure, is not inherent in the chemical molecule, and hence the name Water of Crystallization. The presence of water of crystallization in a salt is expressed by writing after the symbol of the salt, and separated from it by a period, the number of molecules of water with which each salt molecule is associated. Thus we have

$FeSO_4.7\,H_2O$ — Crystallized Ferrous Sulphate, or Green Vitriol.

$Na_2CO_3.10H_2O$ — Crystallized Sodic Carbonate, or Sal Soda.

The same salt, when crystallized at different temperatures not unfrequently combines with different amounts of water of crystallization, the less amounts corresponding to the higher temperatures. Thus manganous sulphate may be crystallized with three different amounts of water of crystallization. We have

$MnSO_4.7H_2O$ when crystallized below 6° C.
$MnSO_4.5H_2O$ " " between 7° and 20°.
$MnSO_4.4H_2O$ " " between 20° and 30°.

The crystalline forms of these three compounds are entirely different from each other; and this fact again corroborates the view that the molecules of water, while a part of the crystalline structure, are not a part of the chemical type of the salt. It will be well to distinguish the molecular aggregate, which the symbols of this section represent, from the simpler chemical molecules by a special term, and we propose to call them crystalline molecules. While, however, there is little room for difference of opinion in regard to the relations in which the molecules of water stand to the structure of most crystals, there are cases where the condition is apparently far less simple, and where we find the water so firmly bound to the salt itself that it seems to form a part of its atomic structure.

QUESTIONS AND PROBLEMS.

1. Analyze reactions [38]. Show what is meant by a metallic hydrate, and define the term *alkali*. Write the similar reactions which may be obtained with lithium, calcium, and rubidium. Name in each case the class of compounds to which the factors and products belong. Also represent these reactions by graphic symbols.

2. Analyze reactions [39]. State the distinction between an alkaline earth and an alkali, and write the similar reactions which may be obtained with barium and strontium. Name in each case the class of compounds to which the factors and products belong. Also represent the reactions by graphic symbols.

3. Analyze reactions [40] and [41], and write the similar reactions which may be obtained with either of the metals calcium, strontium, barium, and magnesium. What theory of the constitution of the metallic hydrates do these reactions suggest?

4. In what respects do the hydrates $Ca{=}O_2{=}H_2$ and $Mg{=}O_2{=}H_2$ differ from $K\text{-}O\text{-}H$ and $Na\text{-}O\text{-}H$?

5. Analyze reactions [42], and show that the principal products must be regarded as hydrates. Name the class of compounds to which the other products and factors belong.

6. State the third theory which is held in regard to the constitution of the hydrates, and write the symbols of the different hydrates according to this view. Also bring these symbols into comparison with those of the same compounds written after the other two plans, and show by means of graphic symbols how far these forms are arbitrary, and how far they represent fundamental differences.

7. In what sense may the solution of ammonia gas in water be regarded as a hydrate? Write reactions [42], using ammonic hydrate instead of the hydrates of sodium, potassium, and barium.

8. In what relation do the metallic oxides stand to the hydrates? Define the term *base*.

9. Define the term *salt*, and illustrate your definition by examples.

10. Define the term *acid*. How does an acid differ from a metallic hydrate? Is an acid necessarily a hydrate? What two classes of acids may be distinguished?

11. What is the distinction between an acid and a basic radical? How are they related to the two hydrogen atoms of water? Assuming that there is no difference between these two atoms in the original molecule of water, does not the replacement of one of the atoms by a radical of either class alter the relations of the second? Is there not an analogy between these phenomena and those of magnetism?

12. Analyze reactions [43 *et seq.*], and point out the evidence of acidity in each case.

13. Analyze the following reactions:—

$$K\text{-}O\text{-}H + HF = KF + H_2O$$

$$Ca{=}O_2{=}H_2 + H_2{=}O_2{=}CO = Ca{=}O_2{=}CO + 2\,H_2O$$

$$Cu{=}O_2{=}H_2 + 2\,H\text{-}O\text{-}NO_2 = Cu{=}O_2{=}(NO_2)_2 + 2\,H_2O$$

$$NaCl + H_2{=}O_2{=}SO_2 = H,Na{=}O_2{=}SO_2 + HCl$$

$$2\,NaCl + H_2{=}O{=}SO_2 = Na_2{=}O_2{=}SO_2 + 2\,HCl$$

Point out the different acids and bases. In what does the evidence of their acidity or basicity appear either in these or in reactions previously given? Show in each case how the replacement of the hydrogen atoms is obtained, and illustrate the difference between the hydrogen atoms of an acid and those of a base. What two classes of acids may be distinguished?

14. Regarding the hydrates as compounds of hydroxyl, how can you define the acids and bases of this class?

15. Represent the composition of nitric, sulphuric, and phosphoric acid by graphic symbols, and show that the two modes of writing their symbols embody essentially the same idea.

16. Hydrochloric acid, acetic acid, nitric acid, hydriodic acid, hydrobromic acid, sulphuric acid, carbonic acid, and phosphoric acid have what basicity? Point out, in the various reactions given in this chap-

ter, the evidence in each case, and write the symbols of the possible sodic salts of the different acids.

17. What class of compounds do the symbols SO_3, N_2O_5, P_2O_5, CO_2, and SiO_2 represent? By a comparison of symbols show how these compounds may be regarded as formed from water, and how they are related to the corresponding acids. To what class of compounds do they stand in direct antithesis?

18. Define the terms *basic* and *acid hydrate*, *basic* and *acid anhydride*, and compare reactions [45] with [40 and 41].

19. Analyze the reaction,

$$BaO + SO_3 = BaO,SO_3.$$

What reason may be urged for writing the symbol of baric sulphate in this way? What was the theory of the dualistic system in regard to such compounds? Represent the symbol by the graphic method, and seek to determine whether the dualistic form is compatible with the theory of molecular unity.

20. The following symbols represent compounds of what class?

$H\text{-}O\text{-}H$	$H_3{\equiv}O_3{\equiv}PO$	$Fe{=}O_2{=}H_2$	$2\,H(HO)$	$(PO_2)_2{=}O$
$K\text{-}O\text{-}H$	$Ca{=}O_2{=}H_2$	$C_2H_5\text{-}O\text{-}H$	$2\,Na\text{-}O\text{-}H$	$(C_5H_9O)_2{=}O$
$H_4{\equiv}O_4{\equiv}Si$	$H\text{-}O\text{-}NO_2$	$H_2{=}O_2{=}SO_2$	$(Fe\text{-}Fe){\equiv}O_3$	$H\text{-}O\text{-}C_2H_3O$
$Ca_2{\equiv}O_4{\equiv}Si$	$K\text{-}O\text{-}NO_2$	$(C_4H_9)_2{=}O$	$Na_2{=}O_2{=}SO_2$	$C_2H_5\text{-}O\text{-}C_2H_3O$

Give in each case the name of the compound so far as you are able to infer it from examples previously given, and show how the symbol is related to that of water.

21. Point out the acid basic and neutral salts among the compounds represented by the following symbols:—

$H, Na{=}O_2{=}CO$	$H, K{=}O_2{=}(C_2O_2)$	$(Hg\text{-}O\text{-}Hg\text{-}O\text{-}Hg){=}O_2{=}SO_2$
$Na_2{=}O_2{=}CO$	$K_2{=}O_2{=}(C_2O_2)$	$[Hg\text{-}Hg]{=}O_2{=}(NO_2)_2$
$H_2, Cu{\equiv}O_4{\equiv}Si$	$Cu{=}O_2{=}(NO_2), H$	$[Fe\text{-}Fe]{\equiv}O_6{\equiv}(SO_2)_3$
$Bi{\equiv}O_3{=}(NO_2), H_2$	$H_2, K{\equiv}O_3{\equiv}As$	$K_2{=}O_2{=}(SO_2\text{-}O\text{-}SO_2)$

What two classes of basic salts may be distinguished? Convert the symbols into the dualistic form.

22. Analyze reactions [45 and 46], and show how far they justify the dualistic form given to the symbols. Represent the same reactions in the graphical form.

23. What class of compounds do the following symbols represent?

$$Ag_3^{\equiv}S_2^{\equiv}As \qquad Ag\text{-}S\text{-}SbS \qquad Ca{=}S_2{=}H_2$$

Write the symbols of the corresponding oxygen compounds.

24. Explain the theory of the colored test-papers, and the use of the terms *acid* and *basic* in connection with them. To what confusion does the double meaning of these terms sometimes lead?

25. The members of the series of alcohols stand in what relation to each other? Does the same relation exist between the members of the series of fat acids, glycols, etc.? Find a general symbol, which will represent the composition of each of these classes of compounds.

26. In what relations do the alcohols stand to the fat acids, and the glycols to the acids derived from them?

27. Select examples from each of the classes of compounds described in §§ 41, 42, and 43, and bring the symbols into comparison with those of some simple hydrate or anhydride with which they exactly correspond.

28. We are acquainted with a class of compounds known as condensed glycols, one of which has the following symbol:—

$$(C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}C_2H_4){=}O_2{=}H_2$$

To what class of salts does this correspond?

29. Judging from the following symbols of a few of the salts of tartaric acid, what conclusion should you reach in regard to the atomicity and basicity of this acid?

$$H_2^{\equiv}O_4^{\equiv}(C_4H_2O_2) \qquad K,H_2^{\equiv}O_4^{\equiv}(C_4H_2O_2) \qquad K_2,H_2^{\equiv}O_4^{\equiv}(C_4H_2O_2)$$

$$(C_2H_5)_2,H_2^{\equiv}O_4^{\equiv}(C_4H_2O_2) \qquad (C_2H_5)_2,(C_2H_3O)_2^{\equiv}O_4^{\equiv}(C_4H_2O_2)$$

30. What is the atomicity and basicity of the different acids whose symbols have been given in this chapter? Does the basicity of the different hydrocarbon acids (§ 41 to § 44) appear to have any connection with the number of oxygen atoms in the radical? Give a definition of atomicity and basicity which applies in all these cases.

31. How do you explain the state of combination of the water which enters into the composition of most crystalline salts? Show by an example how this mode of combination is represented symbolically. What facts may be adduced in support of the opinion that the molecules of water are not a part of the chemical type of the salt?

CHAPTER X.

CHEMICAL NOMENCLATURE.

46. **Origin of Nomenclature.** — Previous to the year 1787 the names given to chemical compounds were not conformed to any general rules; and many of these old names, such as *oil of vitriol, calomel, corrosive sublimate, red precipitate, saltpetre, sal-soda, borax, cream of tartar, Glauber's* and *Epsom salts*, are still retained in common use. As chemical science advanced, and the number of known substances increased, it became important to adopt a scientific nomenclature, and the system which came into use was due almost entirely to Lavoisier, who reported to the French Academy on the subject, in behalf of a committee, in the year named above. In the Lavoisierian nomenclature the name of a substance was made to indicate its composition; and at the time of its adoption, and for fifty years after, it was probably the most perfect nomenclature which any science ever enjoyed. It was based, however, on the dualistic theory, of which Lavoisier was the father; and when at last the science outgrew this theory, the old names lost much of their significance and appropriateness. Within the last few years chemists have attempted to modify the old nomenclature so as to better adapt the names to our modern ideas. Unfortunately, the result, like most attempts to mend a worn-out garment, is far from satisfactory, although it is probably the best which under the circumstances could be attained. The new nomenclature has not the simplicity or unity of the old, and its rules cannot be made intelligible until the student is more or less acquainted with the modern chemical theories. Fortunately, however, the admirable system of chemical symbols supplies the defects of the nomenclature, and for many purposes may be used in its place. We have, therefore, developed this system first, but have

also used, meanwhile, the corresponding scientific names, so that the student might become familiar with the nomenclature, and gather its rules as he advanced. A brief summary of these rules is all that will be necessary here.

47. **Names of Elements.** — The names of the elements are not conformed to any fixed rules. Those which were known before 1787, such as sulphur, phosphorus, arsenic, antimony, iron, gold, and the other useful metals, retain their old names. Several of the elements discovered since that time have been named in allusion to some prominent property, or some circumstance connected with their history; as *oxygen*, from *ὀξὺς γεννάω* (acid-generator); *hydrogen*, from *ὕδωρ γεννάω* (water-generator); *chlorine*, from *χλωρός* (green); *iodine*, from *ἰωδής* (violet); *bromine*, from *βρῶμος* (fetid odor). The names of the more recently discovered metals have a common termination, *um*, as *potassium*, *sodium*, *platinum*; and the names of several of the more recently discovered non-metals end in *ine*, as *chlorine*, *bromine*, *iodine*, *fluorine*. Equally arbitrary names have been given to the compound radicals; but, with a few exceptions, they all terminate in *yl* or *ene*, as *ethyl*, *acetyl*, *hydroxyl*, and *ethylene*, *acetylene*, etc.

48. **Names of Binary Compounds.*** — The simple compounds of the elements with oxygen are called oxides, and the specific names of the different oxides are formed by placing before the word *oxide* the name of the element, but changing the termination into *ic* or *ous*, to indicate different degrees of oxidation, and using the Latin name of the element in preference to the English, both for the sake of euphony and in order to secure more general agreement among different languages. When the same element unites with oxygen in more than two proportions, the Greek numeral prefixes *di*, *tri*, *tetra*, *penta*, etc. are added to the word *oxide*, in order to indicate the additional degrees. Formerly these compounds were called oxides of the different elements, the degrees of oxidation being indicated solely by the prefixes; and, as the old names are still in very general use, they are also given in the following examples.

* Binary compounds consist of two elements; ternary compounds, of three; quaternary compounds, of four.

		New Names.		*Old Names.*
Ag_2O	is	Argentic Oxide	or	Oxide of Silver
N_2O	"	Nitrous Oxide	"	Protoxide of Nitrogen
NO	"	Nitric Oxide	"	Deutoxide of Nitrogen
NO_2	"	Nitric Peroxide	"	Peroxide of Nitrogen
FeO	"	Ferrous Oxide	"	Protoxide of Iron
Fe_2O_3	"	Ferric Oxide	"	Sesquioxide of Iron.

An exception to the above rules is made by some writers in the case of those oxides which, when combined with the elements of water, form acids. As has been already stated, page 109, such compounds are sometimes called anhydrides, the degrees of oxidation being distinguished as before, thus :—

SO_2	is	Sulphurous Oxide	or	Sulphurous Anhydride
SO_3	"	Sulphuric Oxide	"	Sulphuric Anhydride
N_2O_3	"	Nitrous Trioxide	"	Nitrous Anhydride
N_2O_5	"	Nitric Pentoxide	"	Nitric Anhydride
P_2O_3	"	Phosphorous Oxide	"	Phosphorous Anhydride
P_2O_5	"	Phosphoric Oxide	"	Phosphoric Anhydride
CO_2	"	Carbonic Dioxide	"	Carbonic Anhydride
SiO_2	"	Silicic Oxide	"	Silicic Anhydride.

The names in common use, even among chemists, of the earths, the alkaline earths, and the alkaline oxides, make another important exception to the general rules given above, thus :—

Al_2O_3	Aluminic Oxide	is	commonly	called	Alumina
BaO	Baric Oxide	"	"	"	Baryta
SrO	Strontic Oxide	"	"	"	Strontia
CaO	Calcic Oxide	"	"	"	Lime
MgO	Magnesic Oxide	"	"	"	Magnesia
K_2O	Potassic Oxide	"	"	"	Potash
Na_2O	Sodic Oxide	"	"	"	Soda.

The names of the binary compounds of the other elements are formed like those of the oxides.

Compounds of	Chlorine	are	called	Chlor*ides*
" "	Bromine	"	"	Brom*ides*
" "	Iodine	"	"	Iod*ides*
" "	Fluorine	"	"	Fluor*ides*

Compounds of	Sulphur	are	called	Sulph*ides*
"	"	Nitrogen	"	"	Nitr*ides*
"	"	Phosphorus	"	"	Phosph*ides*
"	"	Arsenic	"	"	Arsen*ides*
"	"	Antimony	"	"	Antimon*ides*
"	"	Carbon	"	"	Carbon*ides*.

Moreover, the specific names of the several compounds also follow the analogy of the oxides, thus:—

		New Names.		*Old Names.*
$SnCl_2$	is	Stannous Chloride	or	Protochloride of Tin
$SnCl_4$	"	Stannic Chloride	"	Perchloride of Tin
Fe_2S	"	Diferrous Sulphide	"	Subsulphide of Iron
FeS	"	Ferrous Sulphide	"	Protosulphide of Iron
Fe_2S_3	"	Ferric Sulphide	"	Sesquisulphide of Iron
FeS_2	"	Ferric Disulphide	"	Bisulphide of Iron
CaF_2	"	Calcic Fluoride	"	Fluoride of Calcium.

Here, again, must be noticed certain exceptions to the general rule. Several simple compounds of the elements with hydrogen, of which the hydrogen is easily replaced with a metal or positive radical, are called acids, and retain the specific names of the old nomenclature, thus:—

HCl	or Hydric Chloride	is	called	Hydrochloric Acid
HBr	" Hydric Bromide	"		Hydrobromic Acid
HI	" Hydric Iodide	"		Hydriodic Acid
HF	" Hydric Fluoride	"		Hydrofluoric Acid
H_2S	" Hydric Sulphide	"		Hydrosulphuric Acid.

The last compound is frequently called also sulphuretted hydrogen, and several other hydrogen compounds are named after the same analogy, while others again are usually called by their well-known trivial names, thus:—

H_3Sb	is	Antimoniuretted Hydrogen, also called Stibine
H_3As	"	Arseniuretted Hydrogen, also called Arsine
H_3P	"	Phosphuretted Hydrogen, also called Phosphine
H_3N	"	Ammonia Gas
H_4C	"	Marsh Gas, or Light Carburetted Hydrogen
H_4C_2	"	Olefiant Gas, or, as a radical, Ethylene.

49. **Ternary Compounds.** — Of the old class of ternary compounds, it is only those which are formed after the type of water for which the rules of the nomenclature need at present be explained.

50. **Bases.** — These we call simply hydrates, and for the specific name we take the name of the positive radical, changing the termination into *ic* or *ous*, and using such prefixes as circumstances may require, thus: —

	New Names.		*Old Names.*
$K\text{-}O\text{-}H$	is Potassic Hydrate	or	Hydrate of Potash.
$Ca{=}O_2{=}H_2$	" Calcic Hydrate	"	Hydrate of Lime
$Fe{=}O_2{=}H_2$	" Ferrous Hydrate	"	Hydrate of Protoxide of Iron
$Fe_2^{\equiv}O_6^{\equiv}H_6$	" Ferric Hydrate	"	Hydrate of Sesquioxide of Iron
$Zr^{\equiv}O_4^{\equiv}H_4$	" Zirconic Hydrate	"	Hydrate of Zirconia.

51. **Acids.** — The inorganic acids all take their specific names from the name of the most characteristic element of the negative radical, which is modified by terminations and prefixes as before.

$H\text{-}O\text{-}NO_2$	is called	Nitric Acid
$H_2{=}O_2{=}SO_2$	"	Sulphuric Acid
$H_2{=}O_2{=}SO$	"	Sulphurous Acid
$H_2{=}O_2{=}(S\text{-}O\text{-}S)$	"	Thiosulphurous Acid.

The specific names of the organic acids are, as a rule, arbitrary, like tartaric acid, citric acid, malic acid, gallic acid, uric acid, and the like.

52. **Salts.** — The name of a salt is formed from the name of the acid from which the salt is derived, preceded by the names of the basic radicals. When the name of the acid ends in *ic*, the termination is changed into *ate*; when in *ous*, into *ite*. Moreover, the terminations *ous* and *ic* are retained in connection with the name of the basic radical, and such prefixes are used as may be necessary for distinction, thus: —

New Names.

$Ca''O_2''CO$	is	Calcic Carbonate
$Ca''O_2''(S\overset{II}{O}S)$	"	Calcic Thiosulphite
$Ba''O_2''SO$	"	Baric Sulphite
$Fe''O_2''SO_2$	"	Ferrous Sulphate
$Fe_2'''O_6'''(SO_2)_3$	"	Ferric Sulphate
$(NH_4),Mg''O_3''PO$	"	Ammonio-magnesic Phosphate
$H,(NH_4),Na''O_3''PO$	"	Hydro-ammonio-sodic Phosphate
$H,Na_2''O_3''PO$	"	Hydro-disodic Phosphate
$H_4,Ca^{VI}O_6^{VI}(PO)_2$	"	Tetrahydro-calcic Diphosphate
$Na_2''O_2''B_4O_5$	"	Disodic Tetraborate (Borax).

The terms *acid* and *basic* have been used *as parts of the name* of a salt very confusedly. We would propose to limit this special use of these words to such salts as still contain atoms of hydrogen replaceable by a radical, basic in the first case and acid in the other. This use has been followed on page 110, where the distinction has been pointed out between salts of this class and those basic and acid salts which may be regarded as formed by the cementing together of several radicals into a single complex group. Salts of this last kind we would distinguish by appropriate prefixes, but as examples of names of both forms have already been given on the page cited, it will be unnecessary to multiply them here.

The rules of the nomenclature given above conform to what the author regards as the best present use among chemists. There is, however, an important departure from the general use which must not be overlooked. Several English authors, who think that the adjectives derived from the Latin names of the elements, with the terminations in *ic* and *ous*, are not in harmony with English idioms, use such terms as Gold Chloride, Silver Nitrate, and Iron Sulphate, instead of Auric Chloride, Argentic Nitrate, and Ferrous Sulphate. But although this usage may be safely followed in many cases, it would greatly abridge the capabilities of the nomenclature to express the difference between such compounds as ferrous and ferric chloride, or cuprous and cupric oxides.

In a work designed chiefly for instruction, the writer has thought it best not only to introduce no novelties, but also to represent the actual usage, so far as is possible, in all its phases. He would, however, offer the following suggestions, as guides to the student in selecting for his own use a more uniform and consistent system, hoping that before long the chemists will reach some agreement by which greater uniformity may be secured: — First, that the terminations *ic*, *ous*, *ate*, and *ite*, with the modifying Greek or Latin prefixes, should be used so far as possible to distinguish the different states of quantivalence of the chief multivalent radical of the compound. Secondly, that the Greek numeral prefixes should be used, when necessary, to indicate the number of atoms of any radical which each molecule of such compound contains. Thirdly, that, in forming the name of a compound, it should be the great object to indicate its composition, and that the use of such terms as *acid*, *basic*, or *anhydride*, as parts of the name of a substance, should be avoided.

By referring to the list of sulphates on page 325, and to the list of sulphites on page 321, the student will find good examples of the application of these principles. He will notice that salts in which the quantivalence of sulphur is six are called sulphates, while those in which it is four are called sulphites, and those in which it is two, hyposulphites.

QUESTIONS AND PROBLEMS.

1. Give the names of the compounds represented by the following symbols: —

a. KCl; K_2O; K_2S; K_2O_2SO; $K_2O_2SO_2$; $K_2O_2(S{-}O{-}S)$.

b. FeO; $Fe{=}O_2{=}H_2$; $Fe{=}O_2{=}CO$; $Fe{=}O_2{=}C_2O_2$; $[Fe_2]^{VI}O_3$; $Fe_2^{II}O_2^{II}H_4$; $[Fe_2]^{VI}O_6^{II}(NO_2)_6$.

c. $H{-}Cl$; $H{-}F$; $H{-}O{-}NO_2$; $H{-}O{-}NO$; $H_2{=}O_2{=}SO_2$; $H_2{=}O_2{=}SO$; $H_3{=}O_3{=}PO$.

d. $Hg{=}Cl_2$; $[Hg_2]{=}Cl_2$; $Cu{=}S$; $[Cu_2]{=}S$; PbI_2; KBr; $[Al_2]^{VI}O_3$; ZnO.

e. $H,K{=}O_2{=}SO_2$; $H,Na_2{=}O_3{=}PO$; $H,Na{=}O_2{-}CO$; $H,K{=}O_2{-}(C_2O_2)$.

f. $N{\equiv}N$; N_2O; NO; NO_2; N_2O_3; N_2O_5; MnO; Mn_2O_3; Mn_3O_4; MnO_2.

2. Write the symbols of the following compounds: —

a. Calcic Sulphide; Calcic Sulphite; Calcic Hyposulphite; Calcic Sulphate; Calcic Hydrate; Calcic Sulphohydrate; Calcic Carbonate; Calcic Sulphocarbonate; Calcic Silicate.

b. Water; Potassic Hydrate; Nitric Acid; Potassic Nitrate; Nitric Anhydride; Potassic Oxide.

c. Magnesic Oxide; Magnesic Hydrate; Magnesic Nitrate; Magnesic Carbonate; Magnesic Phosphate; Ammonio-magnesic Phosphate.

d. Cuprous Chloride; Cupric Chloride; Ferrous Chloride; Ferric Chloride; Sulphurous Oxide; Sulphuric Oxide; Phosphorous Oxide; Phosphoric Oxide.

N. B. Examples like the above should be greatly multiplied by the teacher, pains being taken to group together the names and symbols in the way best calculated to exhibit their relations and to assist the memory.

CHAPTER XI.*

MOLECULAR WEIGHTS AND MOLECULAR VOLUMES.

53. **Determination of Molecular Weights.** — The validity of our modern theories of chemistry very greatly depends on the certainty with which molecular magnitudes have been defined, and it is of the first importance for the student of this science to be able to appreciate the relative value of data of this kind. As has been already stated, we do not expect to deduce from the vapor density of a substance the precise value of its molecular weight. *The exact value is determined by the results of chemical analysis, which are, as a rule, far more accurate, and the specific gravity is only used to decide which of several possible multiples must be the true value.*† It has also been shown (§ 24) that we can always calculate the molecular weight of a substance from the results of a chemical analysis, on the assumption that the molecule contains the smallest possible number of whole atoms, and that the true molecular weight must be some simple multiple of this minimum value. Moreover, the general principle has been laid down, that the definite quantities of two or more substances which concur in a chemical process are either in the proportion of the molecular weights of these substances, or of some simple multiples of these weights; and since we can determine by analytical processes these definite proportions with great accuracy, it follows that, when the molecular weight of one of the substances is known, we can readily calculate a corresponding weight for each of the others, and these corresponding

* This chapter is supplementary to the chapter on Molecules, which the student would do well to review in this connection. Although directly connected with the subject of Chapter III., the topics herein discussed involve principles which had not then been developed.

† Compare carefully § 18, and problem 31, page 37.

weights are either the molecular weights of the substances in question, or some simple multiples of these weights, and as between these multiples the vapor density will enable us to decide.

The general principle last stated may be applied in a great variety of ways, which are readily comprehended and best studied in connection with special cases. The most general method is the one previously referred to, which consists in determining the molecular weight approximately from the vapor density, and correcting the result from the percentage composition deduced by chemical analysis (§ 24). But although our modern chemical theories rest in great measure on the molecular weight of a few typical compounds determined, at least approximately, by their specific gravities, yet it is only in a comparatively few cases that we are able to refer the molecular weight of a substance directly to this fundamental measure. Most substances are so fixed, or so easily decomposed by heat, that it is impossible to determine the specific gravity of their vapor, even when such a condition is possible. In these cases, however, we endeavor to refer the molecular weight indirectly to the fundamental measure, by establishing a relation of chemical equivalency between the substance whose molecular weight is sought and some *closely allied* volatile substance whose molecular weight has been previously determined in the manner described above. A few examples will make the application of this principle intelligible.

It is required to determine the molecular weight of nitric acid. A careful study of the numerous nitrates leads to the conclusion that this acid, like hydrochloric acid, *HCl*, contains but one atom of replaceable hydrogen. For example, we find but one potassic nitrate and one sodic nitrate, whereas we should expect to find several, if the acid were polybasic. Hence we conclude that one molecule of argentic nitrate, like one molecule of argentic chloride, *AgCl*, contains but one atom of silver. Next, we analyze argentic nitrate, and find that 100 parts of the salt contain 63.53 parts of silver. We know the atomic weight of silver, 108, and evidently this must bear the same relation to the molecular weight of argentic nitrate that 63.53 bears to 100. But

$63.53 : 100 = 108 : x = 170$, which is the molecular weight of argentic nitrate, and, since the molecule of nitric acid differs from that of argentic nitrate only in containing an atom of hydrogen in place of the atom of silver, its own weight must be $170 - 108 + 1 = 63$.

It is required to determine the molecular weight of sulphuric acid. A comparison of the different sulphates shows that sulphuric acid is dibasic. We find two sulphates of potassium and sodium, an acid sulphate and a neutral sulphate, and hence we conclude that this acid contains two replaceable atoms of hydrogen, and hence that one molecule of neutral potassic sulphate contains two atoms of potassium. In analyzing potassic sulphate it appears that 100 parts of the salt contain 44.83 parts of potassium, and evidently this weight bears the same relation to 100 that the weight of two atoms of potassium bears to the weight of the molecule of potassic sulphate. Thus we have, —

$44.83 : 100 = 78 : x = 174$, the *M. W.* of Potassic Sulphate; and
$174 - 78 + 2 = 98$, the *M. W.* of Sulphuric Acid.

By a similar course of reasoning we may deduce from the results of analysis, and from the general chemical relations, the molecular weight of any other acid or base. If there is any question in regard to the basicity of the acid or the acidity of the base, there will be the same question as to the molecular weight; but we cannot be led far into error, for the true weight will be some simple multiple or submultiple of the one assumed, and the progress of science will sooner or later correct our mistake. From the molecular weight of any acid we easily deduce the molecular weights of all its salts.

When the substance is not distinctively an acid or a base, but is capable of entering into combination with other bodies, we can frequently discover its molecular weight by determining experimentally how much of this substance is equivalent to a known weight of some allied but volatile substance whose molecular weight is known. Thus ammonia gas, whose molecular weight is one of the best-established data of chemistry, enters into

direct union with a compound of platinic chloride and hydrochloric acid ($PtCl_6H_2$) to form a definite crystalline salt whose composition is exactly known.

$$PtCl_6H_2 + 2\,NH_3 = PtCl_6(NH_4)_2 \qquad [49]$$

Now a very large number of substances allied to ammonia form with this same platinum salt equally definite products, so that by simply determining the weight of platinum in these compounds, which is very easily done, their molecular weights may at once be referred to the molecular weight of ammonia.

In discussing this subject it must not be forgotten that, when the percentage and atomic weight of a single constituent of a compound is given, we can always calculate by § 24 a value which is either the molecular weight or some simple submultiple of it; and further, that, if we can also find out the number of atoms of any such constituent in one molecule of the compound, the problem of determining its molecular weight is completely solved. Hence the study of chemical reactions, and all similar investigations by which we seek to discover the chemical relations and molecular structure of bodies, serve also to establish the molecular weight. In such cases as in those previously considered the student must learn by experience the many ways in which the general principles we have enunciated are applied, and the special cases will present little difficulty if only these principles are understood. There are many substances, however, in regard to whose molecular weight we can reach no satisfactory conclusion in the present state of science. This is especially true of the native silicates and other complex compounds of the mineral kingdom. In such cases we adopt provisionally for the molecular weight the value which corresponds to the simplest possible symbol, and wait until the progress of science enables us to reach more definite conclusions.

54. **Constitution of Molecules.** — It is a favorite theory with some chemists that no molecule can exist in a free condition with any of its affinities unsatisfied; but those who hold this view are compelled to admit that two points of attraction in the same atom may, in certain cases, neutralize each other.

Hence they would distinguish between a dyad atom like that of oxygen, $-O-$, with its affinities open, and a dyad atom like that of mercury, Hg, with its affinities closed through their own mutual attraction, like two opposite magnetic poles when in contact. The first could not exist in a free condition, while the last could. In like manner any atom having an even number of points of attraction can exist in a free state, because all its affinities may be satisfied within itself; but an atom having an uneven number of points cannot, for at least one of its affinities must be open. As thus interpreted, it must be admitted that the theory explains many facts.

For example, among the univalent elements, chlorine, and also bromine and iodine when gases, are all known to have molecules consisting of two atoms. So, also, the molecule of cyanogen gas consists of two atoms of the radical CN; and the same is true of ethyl, propyl, etc., at least if the hydrocarbons so named have really the constitution first assigned to them as gases.

Passing next to the dyads, we find that, while oxygen, sulphur, selenium, and tellurium have molecules consisting of two atoms, the metals mercury and cadmium, and the radicals ethylene, propylene (C_2H_4 and C_3H_6), etc., have molecules which coincide with their atoms.

Of the well-defined triad elements none are volatile, but the two triad radicals which have been obtained in a free state — allyl, C_3H_5, and kakodyl, $(CH_3)_2As$ — both have double atomic molecules.

In like manner none of the tetrad elements are volatile, and the only tetrad radicals known in a free state have single atomic molecules.

Of the pentad elements nitrogen has a molecule of two atoms, while phosphorus and arsenic have molecules of four atoms. No compound radicals of this order are known in a free state.

Lastly, the only hexad radical known in a free state, benzol, C_6H_6, has a molecule which coincides with its atom.

Thus it appears that in general the theory is sustained by the facts. Nevertheless there are several well-marked exceptions to it. Thus the well-known compounds $\overset{\text{m}}{NO}$ and $\overset{\text{t}}{NO_2}$ have

molecules which act as radicals of uneven atomicities and yet contain but one complex atom; and certain recent experiments would seem to indicate that at high temperatures it may be possible to dissociate such molecules as *Cl-Cl*, and have the univalent atoms existing by themselves. We must be careful, therefore, not to give too much weight to this hypothesis, but still it may be useful in co-ordinating facts. It leads at once to three general principles which will be found to be almost universally true.

The first is, that the sum of the atomicities of the atoms of every molecule is an even number.

The second is, that the atomicity of any radical is an odd or even number according as the sum of the atomicities of its elementary atoms is odd or even.

The third is, that the quantivalence of elementary atoms must be, as stated on page 81, either even or odd. They are *artiads* or *perissads*, and the theory would lead us to expect that the two characters would never be manifested by the same elements.

It has also been a question among chemists whether molecular combination was possible; in other words, whether it is possible for molecules of different kinds to combine chemically, each preserving its integrity in the compound. Some of the advocates of the unitary theory, in the reaction against the dualistic system, have been inclined to doubt the possibility of such compounds, and have attempted to represent the symbols of *all* compounds in a single molecular group; but any antecedent improbability, on theoretical grounds, is far more than outweighed by the evidence of a large number of compounds whose constitution is most simply explained on the hypothesis of molecular combination. For example, in the crystalline salts it is impossible to doubt that the water exists as such, not as a part of the salt molecule, but combined with it as a whole. So, also, there are a number of double salts whose constitution is most simply explained on a similar hypothesis, and, in the present state of the science, it seems unnecessary to complicate their symbols by forcing them into the unitary mould. It is a characteristic of such molecular compounds as are here assumed, that the force which holds together the molecules is much

feebler than that which binds together the atoms in the molecule. When the molecular attraction is very strong, it is probable that in almost all cases the different molecules coalesce into one; and between the extreme limits we find compounds in which it is difficult to determine whether true molecular combination exists or not. Such coalescing of distinct molecules seems always, however, to be attended with a greater development of heat, and, in general, with a more marked manifestation of physical energies, than usually attends either molecular aggregation or atomic metathesis.

In the notation of this book molecular combination is indicated by writing together the symbols of the different molecules thus united, but separating these symbols by periods. Thus the symbols $2\,KCl\,.\,PtCl_4$ and $3\,NaF\,.\,SbF_3$ represent compounds of this class.

55. **Isomerism, Polymerism, Allotropism, Polymorphism.** — We have already shown that the same atoms may be grouped in different ways, so as to form different molecules which in their aggregation present essentially distinct qualities. Thus arise distinct substances, having the same composition and the same vapor density; and such substances, as has been stated, are said to be isomeric, and the phenomenon is called isomerism. There are different phases of isomerism, which it will be well to distinguish, not so much on account of any essential differences in the phenomena as in order to make ourselves better acquainted with its manifestations.

In the first place, we have examples of isomeric bodies having the same centesimal composition and molecular weight, but whose molecules have an essentially different structure. Thus aldehyde and oxide of ethylene have both the same empirical symbol, C_2H_4O, but the structure of their molecules is indicated by the very different structural symbols

$$\underset{\text{Oxide of Ethylene.}}{(CH_2\text{-}CH_2)\text{-}O} \qquad\qquad \underset{\text{Aldehyde.}}{CH_3\text{-}CO\text{-}H}$$

So also the same empirical symbol $C_3H_6O_2$, and therefore the same centesimal composition and vapor density, are common to

$$\underset{\text{Ethylic Formate.}}{(CH_3\text{-}CH_2)\text{-}O\text{-}(CHO)} \quad \text{and} \quad \underset{\text{Methylic Acetate.}}{CH_3\text{-}O\text{-}(CO\text{-}CH_3)}$$

Such isomeric compounds are essentially distinct substances in all their chemical relations, as their wholly different names indicate.

The second class of isomeric compounds resemble each other far more closely than the last. They have the same general properties and the same general system of reactions, but differ in a few marked qualities, physical or chemical, and preserve these characteristics to a greater or less extent in their derivatives. Such isomers are usually regarded as varieties of the same substance, and are often distinguished by prefixing *ortho*, *para*, or *meta* to a common name. The four varieties of valerianic acid whose structural symbols have been given are good examples of this type of isomeric bodies, and by examining these symbols it will be seen that this type differs from the last only in the fact that the difference of structure is less fundamental.

The third class of isomeric bodies differ solely in their physical relations. Chemically they are the same substances, and are known by the same chemical name, although such isomers are often distinguished by mineralogists as different species. Thus common calcic carbonate crystallizes in two fundamentally distinct forms, corresponding to the two mineralogical species calcite and aragonite, and these differences of form are accompanied by differences of density, hardness, and other physical qualities. Again, titanic oxide occurs in nature in three distinct forms, corresponding to the mineralogical species rutile, brookite, and octahedrite, marked as before by differences of physical qualities. Compounds capable of such different crystalline states are said to be dimorphous, trimorphous, or polymorphous, as the case may be; and our theories lead us to refer the differences to variations in the grouping of the molecules by which the crystalline aggregates are formed, and not to any differences in the molecules themselves.

We may distinguish still a fourth class of isomeric bodies, in which even the physical differences are reduced to a variation in the distribution of certain planes on crystals which are otherwise identical, and to a corresponding difference of optical relations. Thus there are two varieties of tartaric acid, the first

of which deviates the plane of polarization of a ray of light to the left, while the second deviates it to the right, and the similar crystals of the two varieties show certain slight differences in the distribution of their planes; but in almost every other respect the two bodies are identical. Such differences as these are not uncommon, and appear to be even more fundamental than those last described, since they often persist after the substances are brought into solution, when it is probable that the molecules are separated more or less widely. The two varieties of sugar called dextrose and levulose derive their names from the circumstance that an aqueous solution of the first rotates the plane of polarization to the right, while a solution of the second produces a similar effect in the opposite direction, and a well-known process of saccharimetry is based on these effects.

When two substances have the same centesimal composition but different molecular weights, so that the symbol of one is necessarily a simple multiple of that of the other, the substances are said to be polymeric. Thus butyric acid and acetic ether, which are isomeric with respect to each other, are polymeric with respect to oxide of ethylene and aldehyde, as will be seen by comparing the symbols given below:—

$H\text{-}O\text{-}C\text{-}O\text{-}C_3H_7$ (Butyric Acid.)	$C_2H_3\text{-}O\text{-}C\text{-}O\text{-}CH_3$ (Acetic Ether.)
$(CH_2\text{-}CH_2)\text{-}O$ (Oxide of Ethylene.)	$CH_3\text{-}C\text{-}O\text{-}H$ (Aldehyde.)

Among polymeric as among isomeric bodies we find substances, like those just referred to, which differ very widely, and others which are so closely allied that the heavier compounds may be regarded as condensed forms of the lighter; and some chemists confine the use of the term *polymers* to compounds of this last class, like, for example,

C_2H_4O (Aldehyde.) and $C_6H_{12}O_3$ (Paraldehyde.)

Here, however, as before, the differences are all unquestionably due to differences of atomic or molecular structure, although in many cases we have not yet been able to determine in what the difference consists.

Differences of condition similar to those we have described manifest themselves even more markedly among elementary substances; and the word *allotropism* is usually applied in such cases. Thus there are two allotropic states of phosphorus, which differ so much from each other that no one would suspect from their external characters that there was any identity between them, and to these two states correspond two fundamentally different crystalline forms. In some cases the differences between the allotropic states of the same element are far greater than any which are seen between the most unlike isomeric compounds. No substances could be better defined by well-marked and utterly distinct qualities than diamond, plumbago, and charcoal, and yet they are all three allotropic modifications of the one elementary substance we call carbon.

Probably these phenomena are also manifestations of atomic structure. Thus we know that, while a molecule of oxygen gas consists of two oxygen atoms, O_2, a molecule of ozone consists of three, O_3. We know also that, while a molecule of sulphur vapor just above the boiling-point of sulphur consists of six atoms, S_6, a molecule of the same vapor above 860° consists of only two atoms, S_2; and it is a plausible theory that a molecule of diamond differs from one of charcoal in that it consists of a larger number of carbon atoms. Differences of allotropic state may also depend on a difference in the grouping of the same number of atoms, but of such differences we have no positive indications.

56. **Molecular Volumes, Equivalent Volumes, Specific Volumes, Atomic Volumes.** — The fact that all aeriform bodies expand or contract equally under the same variations of temperature or pressure, is intimately connected with that equality of molecular volumes which the law of Avogadro asserts. With liquids and solids no such equality in these physical relations is found, and we should not therefore anticipate that their molecular volumes would be as simply related. Moreover, we have no direct and certain means for determining the relative molecular volumes of liquid and solid bodies. It is true that, if we assume that in such bodies the interspaces are insignificant as compared with the actual volume of the molecules, or bear the same rela-

tion to this volume in all substances, then the quotients obtained by dividing the molecular weights of different bodies by their specific gravities would bear to each other the same relations as the molecular volumes of these bodies. The first of these assumptions is manifestly wholly untenable, and it is equally evident that the second cannot be universally true. Nevertheless, when we compare closely allied substances, we discover interesting relations between the molecular volumes calculated as just described. It is obvious that the absolute values of the quotients obtained by dividing the molecular weights of different bodies by their specific gravities must depend wholly on the units to which the divisors and dividends are referred. But if we assume that the specific gravity of the molecule is the same as the observed specific gravity of the body, or, what amounts to the same thing, that the volume of a molecule is not solely its absolute volume, but includes the whole of that portion of space which it may be said to occupy; then the quotients above described must be proportional to the molecular volumes so defined, and may not inappropriately be called the *molecular volumes* of the bodies, although some authors prefer the terms *equivalent volumes* or *specific volumes*.

Since liquids present a much greater uniformity than solids in their physical condition, we should naturally expect to find simpler relations between their molecular volumes, especially when they are compared as nearly as possible under the same physical conditions, as, for example, at the boiling-points of the several liquids. The specific gravity of a liquid at its boiling-point cannot be ascertained by direct experiment; but when the specific gravity at any one point, for example, 15° C., has been determined, and the rate of expansion is also known, the specific gravity at the boiling-point may be calculated. In this way Professor H. Kopp, of Heidelberg, has determined the molecular volumes of a large number of liquids at the boiling-point, and discovered some remarkable relations between them.

1st. Differences of molecular volume are in numerous instances proportional to the differences between the corresponding chemical symbols. One of the most remarkable examples of this prin-

ciple is the fact that the difference of CH_2 in a series of carbon compounds determines a difference of 22 in the molecular volumes of the successive members of the series.

2d. The replacement of H_2 by O in a chemical compound, when not attended with an essential change of the molecular structure, makes but a slight alteration in the molecular volume.

3d. The replacement of H_2 by C in a chemical compound makes no alteration of molecular volume.

These general principles have furnished the basis for calculating what may be called the atomic volume of the atoms when in combination.

Since the addition of CH_2 to a compound increases the molecular volume by 22, this number may be taken to represent the atomic volume of CH_2. Moreover, since C may take the place of H_2 without altering the molecular volume of the compound, it follows that the atomic volume of C must be equal to that of H_2, and therefore the atomic volume of $C = \frac{22}{2} = 11$; so also that of H_2 is equal to 11, or that of H to 5.5. Further, as the substitution of O for H_2 produces a slight increase in the molecular volume of a compound, the atomic volume of O must be rather greater than 11; and it is found that, by assuming the atomic volume of O under these circumstances to be equal to 12.2, results are obtained agreeing very nearly with those of observation. Such, for example, is the condition of oxygen in the radical acetyl C_2H_3O, which may be regarded as derived from C_2H_5 by a substitution of this kind. But when the oxygen atom occupies the position it has in water, $H\text{-}O\text{-}H$, its atomic volume is smaller. The specific gravity of water at the boiling-point is 0.9579. Hence its molecular volume at that temperature is $\frac{18}{0.9579} = 18.2$; and if the two atoms of hydrogen have a volume of 11, the space left for the oxygen atom is 7.2. Whence we deduce,—

Atomic volume of	C,	11.0
" "	H,	5.5
" "	O (within the radical),	12.2
" "	O (without the radical),	7.8

And by means of these values we can calculate the molecular volumes of a very large number of organic compounds, thus:—

Aldehyde, (C_2H_3O)-H		Alcohol, C_2H_5-O-H		Acetic Acid, C_2H_3O-O-H	
C_2	22.0	C_2	22.0	C_2	22.0
H_4	22.0	H_6	33.0	H_4	22.0
O	12.2	O	7.8	O	12.2
				O	7.8
	56.2		62.8		64.0
Observed, 56.4 at 21°.		Observed, 61.6 at 78°.		Observed, 63.6 at 118°.	

In a similar way, the atomic volumes of several other elements (when in combination) have been determined. Thus we have,—

Atomic volume of	S (within the radical),	28.6
" "	S (without the radical),	22.6
" "	Cl,	22.8
" "	Br,	27.8
" "	I,	37.5
" "	N (in compounds of the ammonia type),	2.3
" "	CN,	28.0
" "	NO_2,	33.0

And, as before, the molecular volumes calculated with these data agree very well with observation. The following are a few examples:—

Oil of Mustard, C_3H_5-NCS		Ethylic Nitrate, C_2H_5-O-NO_2	
$C_3H_5 = 33 + 27.5 =$	60.5	$C_2H_5 = 22 + 27.5 =$	49.5
CN	28.0	O	7.8
S	22.6	NO_2	33.0
	111.1		90.3
Observed at 148°,	113.7	Observed at 86°,	90.1

Although it is evident from the above examples that the same atom may occupy unequal volumes in different positions, and therefore that the molecular volume of a substance depends to a certain extent on the structure as well as on the composition of

the molecule, yet it will also be seen that isomeric compounds must, in most cases, have the same molecular volume; as, for example, acetic acid and methylic formate, common ether and butylic alcohol.

The most general relation that has been observed between the molecular volumes of solid compounds is that isomorphous compounds (§ 31) have equal molecular volumes, which results, of course, when the densities are proportional to the molecular weight. The class of salts called vitriols furnishes a striking illustration of this principle.

Symbols.	Molec. Weight.	Sp. Gr.	Molec. Vol.
$MgSO_4 . 7\,H_2O$	246.0	1.685	146.0
$ZnSO_4 . 7\,H_2O$	287.0	1.953	147.0
$NiSO_4 . 7\,H_2O$	281.0	1.931	145.5
$CoSO_4 . 7\,H_2O$	281.0	1.924	146.0
$FeSO_4 . 7\,H_2O$	278.0	1.884	147.5

To a limited extent a connection has been established between the molecular volume of solids and the elementary substances of which they are composed, similar to that which liquids exhibit when compared as above described; but although certain limited relations have been shown to exist, the subject has not as yet been sufficiently generalized to enable us to present the results without greater amplification than the limit of an elementary text-book allows, and we would refer the student for details to the article on *Atomic Volume* in Watts's Dictionary of Chemistry, to which we are indebted for the material of this section.

QUESTIONS AND PROBLEMS.

1. What are the molecular weights of alcohol and camphor, as deduced from the results of the Sp. Gr. determinations given on page 31, and how do these values agree with the received molecular weights of these substances?

Ans. 45.5 and 155, which, although not closely agreeing with the theoretical numbers, enables us to decide that the symbols of these compounds are C_2H_6O and $C_{10}H_{16}O$, as the simplest interpretation of the analyses would indicate.

2. Calculate the molecular weights of the substances whose vapor densities have been determined in the problems 19 to 30, pages 33 to 37. Compare these results with the received values of the molecular weights, and answer the following questions: —

a. How, in general, were the accepted values found?

b. How far does the vapor density serve to fix the value?

c. On what does the difference between the values deduced from the observed vapor densities and the accepted values depend?

3. A study of the different tartrates has led to the conclusion already expressed, that tartaric acid, although tetratomic, is dibasic. It also appears that 100 parts of neutral argentic tartrate yield, when ignited, 55.39 parts of metallic silver. Required the molecular weight of tartaric acid. Ans. 176.

4. A hundred parts of baric oxide, BaO (whose composition is assumed to be known), yield when treated with sulphuric acid 152.3 parts of baric sulphate. Further it is assumed, as the result of careful study, that sulphuric acid is dibasic, and the metal barium a bivalent radical. Required the molecular weight of sulphuric acid. Ans. 98.

5. The well-known base aniline gives with platinic chloride a definite crystalline product, 100 parts of which yield on ignition 32.99 parts of platinum. Required the molecular weight of aniline. How does this result agree with the Sp. Gr. of aniline vapor, which has been found by observation to be 3.210?

Ans. 93; which corresponds to Sp. Gr. of 3.223.

6. The base triethylamine gives in like manner a platinum salt, 100 parts of which yield on ignition 32.13 parts of platinum. Required the molecular weight. Ans. 101.

7. What is the sum of the atomicities of the atoms of the molecules and radicals represented by the symbols given in the problems 20 and 21, on page 121?

8. Compare together the symbols of the compounds of the various alcohol radicals on pages 114 to 116, and point out the examples of isomerism.

9. Calculate the molecular volumes of the following compounds, from the specific gravities given: —

	Sp. Gr.	Molec. Vol.
Ferrous Chloride,	2.528	50.2
Calcic Chloride,	2.205	50.4
Nickelous Chloride,	2.560	50.6
Mercuric Chloride,	5.320	51.0
Argentic Chloride,	5.517	26.0

10. Calculate the molecular volumes of the following native carbonates: —

		Sp. Gr.
Calcite,	$CaCO_3$	2.72
Dolomite,	$(\frac{1}{2}Ca.\frac{1}{2}Mg)CO_3$	2.85
Magnesite,	$MgCO_3$	3.08
Smithsonite,	$ZnCO_3$	4.42
Rhodochrosite,	$MnCO_3$	3.59
Siderite,	$FeCO_3$	3.80

11. Calculate the molecular volumes of the following liquids at the boiling-point, from the atomic volumes of their elements: —

		Calculated.	Observed.
Benzol,	C_6H_6	99.0	97.9 at 80°
Methylic Oxalate,	$(CH_3)_2{=}O_2{=}C_2O_2$	117.0	116.3 at 162°
Mercaptan,	$C_2H_5{-}S{-}H$	77.6	76.0 at 36°
Chloroform,	$CHCl_3$	84.9	84.8 at 62°
Bromide of Ethylene,	$C_2H_4Br_2$	99.6	99.9 at 130°

12. Calculate and compare the molecular volumes of the following liquids at the boiling-point: —

Ether,	$C_4H_{10}O$	Butylamine,	$C_4H_{11}N$
Butylic Alcohol,	$C_4H_{10}O$	Aniline,	C_6H_7N
Phenol,	C_6H_6O		

CHAPTER XII.

SOLUTION AND DIFFUSION.

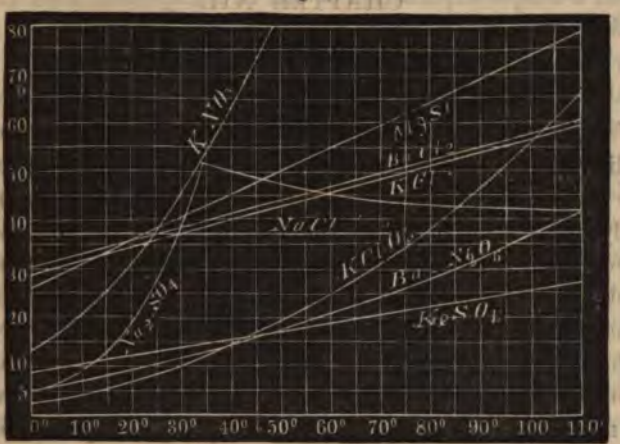
57. **Solution.** — The solvent power of water is one of the most familiar facts of common experience, and all liquids possess the same power to a greater or less degree; but they differ very widely from each other in the manifestation of their solvent power, which for each liquid is usually limited to a certain class of solids. Thus mercury is the appropriate solvent of metals, alcohol of resins, ether of fats, and water of salts. Water is by far the most universal solvent known, and for this reason, as well as on account of its very wide diffusion in nature, it becomes the medium of most chemical changes. The phenomena of aqueous solution form, therefore, a very important subject of chemical inquiry, and these alone will be considered in this connection.

The solvent power of water differs very greatly. Some solids, like potassic carbonate or calcic chloride, liquefy in the atmosphere by absorbing the moisture it contains. Such salts are said to *deliquesce*, and dissolve in a very small proportion of water. Other salts, like calcic sulphate, require for solution several hundred times their weight of water, and others again, like baric sulphate, are practically insoluble.

As a general rule the solvent power of water increases with the temperature; but here, again, we observe the greatest differences between different substances. While the solubility of some salts increases very rapidly with the temperature, that of others increases not at all, or only very slightly; and there are a few which are actually more soluble in cold water than in hot. The solubility of each substance is absolutely definite for a given temperature, and we can determine by experiment the exact amount which 100 parts of water will in any case dissolve.

The results of such experiments are best represented to the eye by means of a curve drawn, as in the accompanying figure, on the principles of analytical geometry.

Fig. 2.



The figures on the horizontal line indicate degrees of temperature, and those on the vertical line parts of salt soluble in 100 parts of water. To find the solubility of any salt for a stated temperature, the curve being given, we have only to follow up the vertical line corresponding to the temperature until it reaches the curve, and then, at the end of the horizontal line which intersects the curve at the same point, we find the number of parts required. These curves also show in each case the law which the change of solubility obeys.

When a liquid has dissolved all of a solid that it can take up at the temperature, it is said to be saturated; but when saturated with one solid, the liquid will still exert a solvent power over others; indeed, in some cases the solvent power is thereby increased. When several salts are dissolved together in water, a definite amount of metathesis seems always to take place, and the different positive radicals are divided between the several acids in proportions which depend on the relative strength of their affinities, and on the quantities of each present. If in this

way either an insoluble or a volatile product is formed, the solid or the gas at once falls out of the solution, and, the equilibrium being thus destroyed, a new metathesis takes place, and this goes on so long as any of these products can be formed. Here, then, we find a simple explanation of the two important laws already stated on page 55.

58. **Solution of Gases.** — Most liquids, but especially water and alcohol, exert on gases a greater or less solvent power, which is marked by differences of manifestation similar to those we have already studied in the case of solids, although the peculiar physical conditions of the gas somewhat modify the result. Under the same conditions, the quantity * of gas dissolved is always the same; but it varies with the pressure of the gas on the surface of the liquid, with the temperature, and with the peculiar nature of the gas and the absorbing liquid. The quantity of gas dissolved by one cubic centimetre of a liquid on which it exerts a pressure of 76 c. m. is called the coefficient of absorption. This coefficient, in almost every instance, diminishes with the temperature; but, as in the case of solids, each substance obeys a law of its own, which must be determined by experiment. The observed values for several of the best known gases, when absorbed by water and alcohol, are given in Chemical Physics, Table VII. With these data we can easily calculate the quantity of any of these gases which a given volume of water or alcohol will absorb, assuming that the gas exerts on the liquid a pressure of 76 c. m. Moreover, since *the quantity of a gas absorbed by a liquid varies directly as the pressure which the gas exerts upon it*, we can easily calculate from the first result the quantity absorbed at any given pressure. Again, it is a direct consequence of the last principle, that at a fixed temperature a given mass of liquid will dissolve the *same volume* of gas, whatever may be the pressure. Lastly, if a mass of liquid is exposed to an atmosphere of mixed gases, it will absorb of each the same quantity as if this gas were alone present, and exerting on the liquid the same pressure which falls to its share

* By quantity of gas is here meant the volume in cubic centimetres measured under the standard conditions of temperature and pressure.

in the atmosphere. The amount dissolved of each gas is easily calculated when the partial pressure and the coefficient of absorption are known. It is thus that water absorbs the oxygen and nitrogen gases of our terrestrial atmosphere; and the fact that these two gases are found dissolved in the ocean in very different proportions from those present in the atmosphere, is a conclusive proof that the air is a mixture, and not, as was formerly supposed, a chemical compound.

59. **Solution and Chemical Change.** — There seems at first sight to be a wide difference between solution and chemical change; for while in the first the solid body becomes diffused through the liquid menstruum without losing its chemical identity or destroying that of the liquid, there is in the second a complete identification of the combining substances in the resulting compound.

The same wide difference appears also between mechanical and chemical solution, which are sometimes confounded by students, because, unfortunately, the same term has been applied to both. When a salt dissolves in water, the differences between salt and solvent are preserved; but when chalk is dissolved in hydrochloric acid, or copper in nitric acid, there is a complete merging of their distinctive qualities in the resulting compound; and the only ground for calling such chemical changes solution is the fact that the solution of the resulting salt in the water, used as the medium of the chemical change, is frequently an essential condition of the process.

But if, instead of comparing extreme cases, we study the whole range of chemical phenomena, we shall find that the distinction is by no means so clearly marked. In many cases what seems to be a simple solution can be shown to be a mixed effect at least of solution and chemical combination; and between this condition of things, where the evidence of chemical combination is unmistakable, and a simple solution, like that of sugar in water, we have every degree of gradation. To such an extent is this true, that the facts seem to justify the opinion that solution is in every case a chemical combination of the substances dissolved with the solvent, and that it differs from other exam-

ples of chemical change only in the weakness of the combining force.

The metallic alloys afford another striking illustration of the same principle. When molten, they may be regarded as solutions of one or more metals in another, but in some cases chemical affinity appears to come into play, and on solidifying they often tend to form definite chemical compounds, and to assume a definite crystalline form.

60. **Liquid Diffusion.** — Closely connected with the phenomena of solution are those of liquid diffusion. These phenomena may be studied in their simplest form, by placing an open vial filled with a solution of some salt in a much larger jar of pure water, as shown in Fig. 3, and so carefully arranging the details of the experiment that the surfaces of the two liquids may be brought in contact without mixing them mechanically. It will then be found that the salt molecules will slowly escape from the vial and spread throughout the whole volume of the water. The rate of the diffusion increases with the temperature equally for all substances, and the whole phenomenon is probably caused by that same molecular motion to which we refer the effects of heat. At best, however, the diffusion is very slow, as we should expect, considering the limited freedom of motion which the liquid molecules possess. It is found, also, that the rate of diffusion differs very greatly for the different soluble salts; but these may be divided into groups of equidiffusive substances, and the rates of diffusion of the several groups bear to each other simple numerical ratios. If a mixture of salts be placed in the vial, it is found that the presence of one salt affects to some degree the diffusion of the other; but if the difference of rate is considerable, a partial separation may be effected, and even weak chemical compounds may be thus decomposed.

Fig 3.

61. **Crystalloids and Colloids.** — There is a very great difference of diffusive power between the ordinary crystalline salts

(including most of the common acids and bases) and such substances as gum, caramel, gelatine, and albumen, which are incapable of crystallizing, and which give insipid viscid solutions, readily forming into jelly; hence the name *colloids*, from κόλλη, glue. The last class is distinguished by a remarkable sluggishness and indisposition to diffusion; as is illustrated by the fact that sugar, one of the least diffusible of the crystalloids, diffuses seven times more rapidly than albumen, and fourteen times more rapidly than caramel. Our theories would lead us to believe that this great difference of diffusive power is caused by the fact that the molecules of colloids are far more complex atomic aggregates than those of crystalloids, and therefore are heavier and move more slowly. Moreover, the diffusive power is only one of many characters which point to a great molecular difference between these two classes of substances.

62. **Dialysis.** — The difference of diffusive power between the two classes of compounds distinguished in the last section is still further increased when the aqueous solution is separated from the pure water by some colloidal membrane; and upon this fact Professor Graham of London, to whom we owe our whole knowledge of this subject, has based a simple method of separating crystalloids from colloids, which he calls dialysis.

A shallow tray is prepared by stretching parchment paper (which is itself an insoluble colloid) over one side of a gutta-percha hoop, and holding it in place by a somewhat larger hoop of the same material. The solution to be *dialyzed* is poured into this tray, which is then floated on pure water whose volume should be eight or ten times greater than that of the solution. Under these conditions the crystalloids will diffuse through the porous septum into the water, leaving the colloids in the tray, and in the course of two or three days a more or less complete separation of these two classes of substances will have taken place.

In this way arsenious acids and similar crystalloids may be separated from the colloidal materials, with which, in cases of poisoning, they are frequently found mixed in the stomach; and by an application of the same method alumina, ferric oxide, chromic oxide, stannic, metastannic, titanic, molybdic, tungstic,

and silicic acids have all been obtained dissolved in water in a colloidal condition. All these substances usually exist in a crystalline condition. The colloidal condition appears to be an abnormal state, and in almost all such substances there is a tendency towards the crystalloid form.

63. **Diffusion of Gases.** — Gases diffuse much more rapidly than liquids, as we should naturally expect from the greater freedom of motion which their molecules possess. Moreover, if the theory of the molecular condition of gases is correct, we ought to be able to calculate the relative rates of diffusion of different gases from their respective molecular weights. If it is true, as stated on page 17, that at any given temperature

$$\tfrac{1}{2} m V^2 = \tfrac{1}{2} m' V'^2,$$

then it follows that

$$V : V' = \sqrt{\tfrac{1}{2} m'} : \sqrt{\tfrac{1}{2} m} = \sqrt{\text{Sp. Gr.}'} : \sqrt{\text{Sp. Gr.}}$$

Hence, if two masses of gas are in contact, the molecules of either gas must move into the space filled by the other with velocities which are inversely proportional to the square roots of the respective specific gravities. If one gas is hydrogen (Sp. Gr. = 1), and the other oxygen (Sp. Gr. = 16), the molecules of hydrogen must move past the section separating the two masses four times as rapidly as those of oxygen; and since all gas molecules occupy the same volume, it follows, further, that four volumes of hydrogen must enter the space filled by the oxygen, while one volume of oxygen is passing in the opposite direction. Numerous experiments have fully confirmed this theoretical deduction, and the close agreement between theory and experiment furnishes important evidence in favor of the theory itself. Such experiments can be made, moreover, with great accuracy, since the molecular motion is not arrested by various porous septa, which may be used to separate the two masses of gas, and which entirely prevent the passage of gas currents that might otherwise vitiate the results.

CHAPTER XIII.

RELATIONS OF THE ATOMS TO HEAT.

Atmosphere. — The earth is surrounded by an ocean matter called the atmosphere, and many of the most chemical changes which we witness in nature are by the reaction of this atmosphere on the substances surrounds and bathes. The great mass of the atmosnsists of the two elementary gases, oxygen and nitrogen, together in the proportions indicated in the following

Air contains	By Volume.	By Weight.
Oxygen,	20.96	23.185
Nitrogen,	79.04	76.815
	100.00	100.000

hat the air is a mixture, and not a chemical compound, is ved by the action of solvents upon it (§ 58); but, neverthe, the analyses of air collected in different countries and at erent heights in the atmosphere show a remarkable conancy in its composition. Besides these two gases, which make over 93 per cent of its whole mass, the air always contains ariable quantities of aqueous vapor, carbonic dioxide, and amnonia, and sometimes also traces of various other gases and vapors.

65. Burning. — Of the two chief constituents of the atmosphere, nitrogen gas is a very inert substance, and serves chiefly to restrain its more energetic associate. Oxygen gas, on the other hand, is endowed with highly active affinities, and tends to enter into combination with other elementary substances, and with many compounds which are not already saturated with this all-pervading element. Many of these substances, such as

phosphorus, sulphur, petroleum, coal, and wood, have such a strong affinity for oxygen, that under certain conditions they will absorb it from the atmosphere, and combine with it under the evolution of heat and light. These substances are said to be combustible, and the process of combination is called combustion. Moreover, all burning with which we are familiar in common life consists in the union of the burning body with the oxygen of the air. The chemical process in these cases may be expressed, like any other chemical reaction, in the form of an equation.

Burning of Hydrogen Gas.

$$\overset{\text{Hydrogen Gas.}}{2\,H\text{-}H} + O\text{-}O = \overset{\text{Aqueous Vapor.}}{2\,H_2O} \qquad [50]$$

Burning of Carbon (Charcoal).

$$\overset{\text{Carbon.}}{C} + O\text{-}O = \overset{\text{Carbonic Anhydride.}}{CO_2} \qquad [51]$$

Burning of Benzol.

$$\overset{\text{Benzol.}}{2\,C_6H_6} + 15\,O\text{-}O = 12\,CO_2 + 6\,H_2O \qquad [52]$$

Burning of Alcohol.

$$\overset{\text{Alcohol.}}{C_2H_6O} + 3\,O\text{-}O = 2\,CO_2 + 3\,H_2O \qquad [53]$$

Burning of Sulphur.

$$2\,S + 2\,O\text{-}O = \overset{\text{Sulphurous Anhydride.}}{2\,SO_2} \qquad [54]$$

Burning of Phosphorus.

$$P_4 + 5\,O\text{-}O = \overset{\text{Phosphoric Anhydride.}}{2\,P_2O_5} \qquad [55]$$

Burning of Magnesium.

$$2\,Mg + O\text{-}O = \overset{\text{Magnesic Oxide.}}{2\,MgO} \qquad [56]$$

The four substances, hydrogen gas, charcoal, benzol, and alcohol, may be regarded as types of our ordinary combustibles; and, as the first four reactions show, the products of their combustion are all aeriform. Moreover, these products are wholly devoid of any sensible qualities, and hence the apparent annihilation of the burning substance, and the reason that for so long a period

the nature of the process remained undiscovered. That these qualities of the products of ordinary combustion are not necessary conditions of the process, but remarkable adaptations in the properties of those combustibles which are our artificial sources of light and heat, is shown by the fact, that in the last two reactions the products of the combustion are solids, while in [54] the product is a noxious suffocating gas.

A careful inspection of the reactions will also teach the student several other important facts in regard to the processes here represented. It will be seen that in the burning of hydrogen gas two volumes of hydrogen gas and one volume of oxygen gas combine to form two volumes of aqueous vapor. It will further be noticed that in the burning of carbon and of sulphur a given volume of oxygen gas yields in each case its own volume of the aeriform product. The carbon in the one case, and the sulphur in the other, are absorbed, as it were, by the gas, without any increase of volume. Further, if the experiments are made, which these reactions represent, it will appear that, in all those cases where the combustible is represented as a gas, the combustion is accompanied by flame, while in the case of carbon, which is a fixed solid, there is no proper flame. Hence we learn that flame is burning gas, and that only those substances burn with flame which are either gases themselves, or which, at a high temperature, become volatilized, or generate combustible vapors. Still other important facts connected with the process of combustion will be learned by solving the following problems, according to the rules already given (§§ 25 and 26).

PROBLEMS.

1. How many cubic centimetres of hydrogen gas, and how many of oxygen gas, are required to form one cubic centimetre of liquid water? *

Ans. 1,240 $\overline{\text{c. m.}}^3$ of hydrogen gas, and 620 $\overline{\text{c. m.}}^3$ of oxygen gas.

2. How many cubic metres of air are required to burn 448 kilogrammes of coal, assuming that the coal is pure carbon?

Ans. 833.333 $\overline{\text{m.}}^3$ of oxygen gas, or 3,975.83 $\overline{\text{m.}}^3$ of atmospheric air.

* Here, as in all other problems throughout the book, it is understood, unless otherwise expressly stated, that the measurements and weights are all taken at the standard temperature and pressure. (Compare §§ 11 and 14.)

3. How many cubic metres of carbonic dioxide are formed by the burning of 1,000 kilogrammes of coal, assuming, as before, that the coal is pure carbon? Ans. 1,860 m^3.

4. How many litres of carbonic dioxide, and how many of aqueous vapor, would be formed by burning one litre of benzol vapor?

Ans. Simple inspection of the equation shows that 6 litres of the first and 3 litres of the second would be formed.

5. How many litres of carbonic dioxide, and how many of aqueous vapor, would be formed by burning one litre of liquid alcohol (C_2H_6O)? *Sp. Gr.* of liquid at $0° = 0.815$.

Ans. One litre of alcohol weighs 815 grammes, or 9,097 criths; and since the Sp. Gr. of alcohol vapor is 23, this quantity of liquid would yield 395.6 litres of vapor. Hence there would be formed $2 \times 395.6 = 791.2$ litres of carbonic dioxide, and $3 \times 395.6 = 1{,}186.8$ litres of aqueous vapor.

66. **Heat of Combustion.** — The reactions of the last section represent only the chemical changes in the processes of burning. The physical effects which accompany the chemical changes our equations do not indicate, but it is these remarkable manifestations of power which chiefly arrest the student's attention, and on this power the importance of the processes of combustion as sources of heat and light wholly depends.

The immediate cause of the power developed in the process of combustion is to be found in the clashing of material atoms. Urged by that immensely powerful attractive force we call chemical affinity, the molecules of oxygen in the immediately surrounding atmosphere rush, from all directions and with a very great velocity, upon the burning body. The molecules of oxygen thus acquire an enormous moving power; and when, at the moment of chemical union, the onward motion is arrested, this moving power is distributed among the surrounding molecules, and is manifested in the phenomena of heat and light.* (Compare § 13.)

* According to our best knowledge, the phenomena of light are merely another manifestation of the same molecular motion which causes the phenomena of heat. When we speak of the amount of heat produced, we refer always to the total amount of molecular motion; although, even in the most brilliant illumination,

The quantity of heat evolved during combustion varies very greatly with the nature of the combustible employed, but it is always constant for the same combustible if burnt under the same conditions, and is exactly proportional to the weight of combustible consumed. We give in the following table the amount of heat evolved by *one kilogramme* of several of the most common combustibles when they are burnt in oxygen gas in their ordinary physical state. The numbers represent what is called the calorific power of the combustible. With the exception of the last two, which are only approximate values, necessarily varying with the different varieties of those combustibles, the values are deduced from the very accurate experiments made by Favre and Silbermann.

Calorific Power of Combustibles.[*]

	Units.		Units.
Hydrogen,	34,462	Sulphur,	2,221
Marsh Gas,	13,063	Wood Charcoal,	8,080
Olefiant Gas,	11,858	Carbonic Oxide,	2,400
Ether,	9,027	Dry Wood, (about)	3,654
Alcohol,	7,184	Bituminous Coal, "	7,500

The calorific power of our ordinary hydrocarbon fuels may be calculated approximately when their composition is known. Most of these combustibles contain more or less oxygen, and it is found that the amount of heat developed by the perfect combustion of the fuel is equal to that which would be produced by the perfect combustion of all the carbon, and of so much of the hydrogen as is in excess of that required to form water with the oxygen present. The rest of the hydrogen may be regarded, so far as relates to the present problem, as in combination with oxygen in the state of water; and in estimating the available heat

the amount of mechanical power manifested as light appears to be inconsiderable as compared with that which takes the form of heat.

[*] It must be carefully noted that the values in this table give in each case the calorific power of one kilogramme of the combustible, and do not therefore coincide with the values given further on, which, though deduced from the same experimental data, are calculated on a different basis.

produced, we must deduct the amount of heat required to convert not only this water into steam, but also any hygroscopic water which may be present. Moreover, if we use in our calculation the value of the calorific power of hydrogen given in the table on page 159, we must also deduct the amount of heat required to convert into vapor all the water formed in the process of burning, because, in the experiments by which this value was obtained, the aqueous vapor formed was subsequently condensed to water and gave out its latent heat.

PROBLEM.

Given the average composition of air-dried wood as in the table, to find the calorific power.

Carbon,	400	From the results of analysis we easily deduce	
Hydrogen,	48	Quantity of H in combination with O,	41
Oxygen,	328	" " available as fuel,	7
Nitrogen and Ash,	24	Quantity of water formed by burning 48 parts of hydrogen,	432
Hygroscopic Water,	200	Hygroscopic Water,	200
	1000	Total quantity of water evaporated,	632

	Units of Heat.
400 grammes of carbon yield	3,232
7 " " hydrogen yield	241
	3,473
Deduct amount of heat required to convert 632 grammes of water into vapor (see § 15)	339
Calorific power of air-dried wood	3,134

From the mechanical equivalent of heat given on page 18, and from the data of the above table, we can easily calculate the mechanical power developed in ordinary combustion; and the student will be surprised to find how great this power is. The burning of one kilogramme of charcoal produces an amount of heat which is equivalent to $8,080 \times 423 = 3,417,840$ kilogramme metres; that is, the moving power which is developed by the clashing of the atoms during the combustion of this small amount of coal is equal to that which would be produced by the fall of a mass of rock weighing 8,080 kilogrammes over a precipice 423

metres high; and could this power be all utilized, it would be adequate to raise the same weight to the same height, or to do any other equivalent amount of work. The steam-engine is a machine for applying this very power to produce mechanical results; but, unfortunately, in the best engines we do not utilize much more than one twentieth of the power of the fuel; and to find a more economical means of converting heat into mechanical effect is one of the great problems of the present age.

67. **Calorific Intensity.** — The calorific intensity of fuel is to be carefully distinguished from its calorific power. By *calorific power* is meant, as we have seen, the total quantity of heat developed by the combustion of a given amount of fuel. By *calorific intensity* we mean the maximum temperature developed in the process of combustion. Provided the products are the same, the total amount of heat produced in any case is not influenced by the rapidity of the process; but it is evident that the temperature of the burning fuel will depend, other things being equal, on the rapidity with which the heat is developed as compared with the rapidity with which it is dissipated through surrounding bodies; and when the combination with oxygen is very slow, the heat may be dissipated as fast as it is generated, and then the temperature of the burning body will not rise above that of the surrounding atmosphere, as is the case in many of the processes of slow combustion.

Assuming, however, that all the heat is retained by the products of combustion, we can calculate the maximum temperature which can in any case be produced, provided the calorific power of the fuel and the specific heat of the products of combustion are known. The calorific intensity is simply the temperature to which the heat generated by the burning of each portion of the fuel can raise the products of its own combustion. Assume that the quantity burnt is one kilogramme, that the calorific power or number of units of heat produced is C, that the weights of the various products of combustion are W, W', W'', etc., and that the specific heats of these products are S, S', S'', etc. Then $WS + W'S' + W''S''$ + etc. represents the amount of heat required to raise the temperature of the whole mass of the products

one centigrade degree (§ 17), and the maximum temperature to which these products can be raised in the process of combustion must be

$$T = \frac{C}{WS + W'S' + W''S''} \qquad [57]$$

PROBLEMS.

1. Find the calorific intensity of charcoal burnt in pure oxygen, and also in air under constant atmospheric pressure.

Solution. By [51] we easily find that each kilogramme of carbon yields, by burning, 3.67 kilogrammes of carbonic dioxide, which is the sole product of its combustion when burnt in pure oxygen. The specific heat of carbonic dioxide (Chem. Phys. 235) is 0.2164. The calorific power of charcoal is 8,080. By substituting these values in [57] we get $T = 10{,}174°$.

When the charcoal burns in air, the 3.67 kilogrammes of carbonic dioxide formed by the combustion are mixed with a large mass of inert nitrogen, which must be regarded as one of the products of the combustion. The weight of this nitrogen is easily calculated from the known composition of air by weight (§ 64) and from the amount of oxygen consumed in the process.

$$23.2 : 76.8 = 2.67 : x\,; \text{ or } x = 2.67 \times 3.31 = 8.84.$$

We have now, besides the values given above, $W' = 8.84$ and S', the specific heat of nitrogen, equal to 0.244. Whence $T' = 2{,}738°$.

2. Find the calorific intensity of hydrogen gas burnt in oxygen and burnt in air.

Solution. One kilogramme of hydrogen yields 9 kilogrammes of aqueous vapor. The specific heat of aqueous vapor is 0.4805. The calorific power of hydrogen is not so great when the gas is burnt under ordinary conditions as that given in the table on page 159; for in the experiments of Favre and Silbermann the vapor formed by the combustion was subsequently condensed to water, and gave out its latent heat, while in a burning flame of hydrogen no such condensation takes place. Hence $C = 34{,}462 - (537 \times 9) = 29{,}629$. We also have $W = 9$ and $S = 0.480$. Whence $T = 6{,}853°$.

When hydrogen is burnt in air, the nitrogen, mixed with the aqueous vapor, weighs 26.49 kilogrammes, and S' is the same as in the previous problem. Whence $T' = 2{,}746°$.

It appears then from these problems, that, although the calorific power of hydrogen is much greater than that of carbon, its calorific intensity is less. But it must be remembered that the conditions assumed in these problems are never realized in practice, for the heat generated by the combustion is never wholly retained in the products. The process of combustion requires a certain time, and during this time a portion of the heat escapes. Moreover, more air passes through the combustible than is required for perfect combustion, and many of the data which enter into the calculation are uncertain. The results, therefore, can only be regarded as approximate. The theoretical conditions are most nearly realized in a gas flame, and especially in that form of burner known as the Bunsen lamp. The temperature of the flame of this lamp, when carefully regulated, is very nearly that which the theory would assign.

68. **Point of Ignition.** — In order that a combustible body should take fire, and continue burning in the atmosphere, it must be heated to a certain temperature, and maintained at this temperature. This temperature is called the point of ignition; and although it cannot always be accurately measured, and is undoubtedly more or less variable under different conditions, yet, nevertheless, it is tolerably constant for each substance. For different substances it differs very greatly. Thus phosphorus takes fire below the boiling-point of water, sulphur at 260°, wood at a low red reat, anthracite coal only at a full red heat, while iron requires the highest temperature of a forge. If a burning body is cooled below its point of ignition, it goes out; and our ordinary combustibles continue burning in the air only because the heat evolved by the burning maintains the temperature above the required point. If the temperature of the combustible is not maintained sufficiently high, either because the chemical union is too slow, or because the calorific power is too small, then the combustible will not continue to burn in the air of itself, although it may burn most readily if its temperature is sustained by artificial means. Hence many of the metals which will not burn in the air burn readily in the flame of a blowpipe, and an iron watch-spring burns like a match in an atmosphere of

pure oxygen. The calorific intensity of all combustibles when burnt in the atmosphere is, as we have seen, greatly reduced by the presence of nitrogen; and hence it is that, although the burning watch-spring is maintained above the point of ignition in pure oxygen, it soon falls below this temperature, and goes out when ignited in the air. Thus it is that the nitrogen of our atmosphere exerts a most important influence on the action of the fire element; and it can easily be seen that, were it not for these provisions in the constitution of nature, by which the active energies of oxygen are kept within certain limits, no combustible material could exist on the surface of the earth.

69. **Calorific Power derived from the Sun.** — The great mass of the crust of our globe consists of saturated oxygen compounds, or, in other words, of burnt materials; and the total amount of combustible materials which exists on its surface is comparatively very small. That which exists naturally consists almost entirely of carbon and its compounds, such as coal, naphtha, and wood; and all these substances are the results of organic growth, either of the present age or of earlier geological epochs. Moreover, whatever subsequent changes the material may have undergone, it was all originally prepared by the plant from the carbonic dioxide and water of our atmosphere; for, in the economy of nature, these products of combustion have been made the food of the vegetable world. The sun's rays, acting on the green leaves of the plant, exert a mysterious power, which decomposes carbonic dioxide, and perhaps also water; and, as the result of this process, oxygen is returned to the atmosphere, while carbon and hydrogen are stored up in the growing tissues of the plant. The sun thus undoes the work of combustion, and parts the atoms which the chemical affinities had drawn together. In doing this, the sun exerts an enormous power, and the work which it thus accomplishes is the precise measure of the calorific power of the combustible material which it then prepares. When we wind up the weight of a clock, we exert a certain power which reappears in its subsequent motions; and so, when the sun's rays have parted these atoms, the great power it exerts is again called into action, when in the process of combustion the atoms reunite. Moreover,

what is true of calorific power is true of all manifestations of power on the surface of the earth. Every form of motion is sustained by the running down of some weight which the sun has wound up; and, according to the best theory we can form, the sun's power itself is sustained by the gradual falling of the whole mass of the solar system towards its common centre. However varying in its manifestation, all power in its essence is the same, and the total amount of power in the universe is constant.

This great generalization, which is now regarded as a fundamental principle of physical science, is called the Conservation of Energy. It is, without doubt, the correlative of the equally important principle which we have already discussed, that the weight of matter remains invariable, however great the physical or chemical changes it undergoes; and this last principle, which implicitly underlies all chemical reasoning, we have already elsewhere named the Conservation of Mass.

THERMO-CHEMISTRY.

70. **Heat of Chemical Action.** — The heat of combustion is only a striking manifestation of a very general principle, which holds true in all chemical changes. It would appear that whenever, in a chemical reaction, atoms or molecules are drawn together by their mutual affinities, a certain amount of moving power is developed, which takes the form of heat; and whenever, on the other hand, these same atoms or molecules are drawn apart by the action of some superior force, the same amount of moving power is expended, and heat disappears. Every chemical reaction is a mixed effect of such combinations and decompositions; and when the effect of each analysis and synthesis is known, it is possible to calculate what must be, in any case, the total thermal result. During the last ten years there has been accumulated a very large mass of experimental data on which such calculations can be based, and thus has arisen a new department in the science of chemistry which has been called Thermo-Chemistry. The general principles of this subject may be summed up in the two following propositions: —

First. Whenever a system of bodies undergoes chemical or physical changes, and passes into another condition, whatever may have been the nature or succession of the changes, the quantity of heat evolved or absorbed depends solely on the initial and final conditions of the system, provided no effect has been produced on bodies outside.

Second. In any reaction between a system of bodies not acted upon by external agents, the tendency is towards that condition and those products which will result in the greatest evolution of heat.

In the investigations of thermo-chemistry, these principles present themselves under so many unexpected and surprising phases, that it becomes important to state the following subordinate propositions, although they are all direct deductions from the general principles just stated; and, indeed, these general principles are included under that still wider generalization, the conservation of energy.

1. The heat absorbed in the decomposition of a compound is equal to the heat evolved in its formation, provided the initial and the final states are the same. In the case of wood, for example, the products of its combustion are the food of the growing plant, and hence, since the initial and final states are the same, we are justified in the conclusion previously stated, that the heat absorbed in the process of vegetable growth is equal to the amount evolved during the burning of the resulting wood.

2. The heat evolved in a series of successive chemical changes is equal to the sum of the quantities which would be evolved in each separately, provided the final conditions are the same. Hence it is that, when a compound cannot be formed by the direct union of its elements, we can determine the heat of combination, as it is called, by measuring the calorific effects in the several stages of the indirect processes by which they are prepared.

3. In any series of chemical changes, when the initial and final conditions are the same, the total thermal effect is the same, however different the processes by which the result may be reached. Hence, when the thermal effect of a given chemical reaction cannot be directly measured, we can often reach the result indirectly in the following way. We arrange two systems of reactions, both of which begin with the same factors in the same conditions, and end with the same pro-

ducts in the same conditions. In one of these series of reactions there must be no process whose thermal result, if not already known, cannot be measured with the calorimeter. In the other series the chemical combination, or decomposition, whose thermal effect we are investigating, enters as an unknown term, the effect of the other chemical changes involved being known or capable of measurement, as in the first series. It follows now, from the principle we are discussing, that, if we subtract the sum of the quantities measured in the second series from the sum of those measured in the first series, we shall have the value of the unknown quantity. An excellent example of this method will be given on page 172.

4. The difference between the quantities of heat evolved in two series of changes, starting from two different states but ending in the same final state, is equal to that evolved or absorbed in passing from one initial condition to the other; or, conversely, the difference between the quantities of heat evolved in two series of changes, starting from the same initial condition but ending in two different states, is equal to that which would be evolved or absorbed in passing from one of the final conditions to the other. Thus the heat of formation of a compound of hydrogen and carbon can be ascertained by measuring the heat of combustion of the hydrocarbon; for, as the final states are the same, whether we burn the hydrocarbon or an equivalent amount of charcoal and hydrogen gas, the thermal difference between the hydrocarbon on the one hand and the charcoal and hydrogen gas on the other must be equal to the difference between the heat of combustion of the compound and the sum of the similar values for the two combustible elementary substances, which have been accurately measured. So, also, to determine the heat evolved in the reaction

$$SO_3 + H_2O = H_2SO_4,$$

we have only to dissolve in one experiment SO_3 and in another H_2SO_4, in a comparatively large amount of water, when the difference in the heat evolved in the two cases will be the quantity required.

5. When a compound gives up one of its elements to another body, the heat evolved in the reaction is the difference between the heat of formation of this compound and that of the resulting product. Thus, in the familiar processes where water holding chlorine in solution is used as an oxidizing agent, the water gives up its hydrogen to the chlorine, forming hydrochloric acid, and the heat evolved is the difference

between the heat of formation of H_2O and $2\,HCl$. This reaction is, of course, accompanied by others, in which the oxygen liberated does a specific work and produces a specific thermal effect, but of this no account is here taken.

Theorems of this sort might be very greatly multiplied, as they have been by Berthelot, in his work on thermo-chemistry;* but the above will give the student a general idea of the scope and possibilities of the subject.

71. **Calorimetry.** — The methods of determining the amount of heat evolved during any chemical or physical change are in theory very simple, and form a branch of experimental science known under the name of Calorimetry. In most cases the process is conducted in a vessel surrounded with water, or in the water itself, which, in so many chemical experiments, is the medium of the chemical change; and in either case, if we know the weight of the water, and carefully measure the number of degrees through which its temperature is raised, we can at once estimate the amount of heat evolved. Of course, the water itself must be held in some vessel; and although this is made of polished metal, as light as possible, and carefully insulated from all external thermal influences, nevertheless, as the vessels used necessarily partake of the temperature of the water, they must absorb a portion of the heat evolved. But, knowing the weight and specific heat of the material of the vessels, it is easy to calculate the weight of water which would be their thermal equivalent, and this we add as a correction to the weight of actual water taken. We thus obtain as our experimental result a certain number of grammes of water raised in temperature a certain number of centigrade degrees, and the product of the two gives the number of units of heat evolved. It is necessary to measure the change of temperature with great care to the twentieths, or even to the hundredths, of a centigrade degree, and to adapt the apparatus to the various conditions which such determinations impose. We must refer, however, to the work of Berthelot just noticed for descriptions

* Essai de Mécanique Chimique, par M. Berthelot, Paris, 1879.

of apparatus and methods of experimenting, and to the author's work on Chemical Physics, for a fuller statement of the theory of calorimetry.

72. **Methods of Investigation.** — The problem with which thus far the investigators of thermo-chemistry have been chiefly occupied is, starting from the elementary substances, to determine the heat of combination of various compounds; for example, starting with solid sulphur and with oxygen and hydrogen gases, to determine the heat evolved in the production of sulphuric acid, H_2SO_4. In this case, as with most chemical compounds, the product cannot be formed by a direct chemical combination; and even when direct union is possible, it is seldom that the heat of combination can be directly measured with a calorimeter. Indeed, by far the larger number of chemical processes do not fulfil the conditions which an accurate measure of the accompanying thermal change involves, and a vast amount of chemical knowledge and ingenuity has been shown in devising indirect methods by which the result may be reached.

The following examples will illustrate not only the method, but also the manner in which the general principles stated in the last section are applied, and the results calculated.

Berthelot calculated the heat of formation of sulphuric acid (H_2SO_4) from the following experimental data: —

First. The amount of heat developed by burning a weighed amount of sulphur, as determined by Berthelot himself. As usual in such cases, the result is stated in terms which are proportional to the molecular weights of the substances involved in the reaction, thus: —

(1) $\mathrm{S} + \mathbb{O}_2 = \mathbb{SO}_2$ evolves 69,000°.

And by this is meant that 32 grammes of sulphur in combining with 32 grammes of oxygen gas give off sufficient heat to raise the temperature of 69,100 grammes of water one centigrade degree, or 69,100 units of heat as defined in the last section; but it should be noticed that these units are one thousand times smaller than the units defined in § 13. This method of stating

results enables us to carry our calculations through successive reactions without constant reductions.*

Second. The amount of heat developed by the solution of sulphurous oxide gas in water which had been determined both by Favre and by Thomsen: —

(2) $\mathbb{SO}_2 + H_2O + Aq = (H_2SO_3 + Aq)$ evolves 7,700^c.

Third. The amount of heat developed in the following reaction, as determined by Thomsen: —

(3) $(H_2SO_3 + H_2O + Aq) + \mathbb{Cl}_2 = (H_2SO_4 + 2\,HCl + Aq)$ 73,900^c.

Fourth. The heat developed by burning chlorine in dry hydrogen, as determined by Thomsen: —

(4) $\mathbb{H}_2 + \mathbb{Cl}_2 = 2\,\mathbb{HCl}$ evolves 44,000^c.

Fifth. The heat developed by dissolving hydrochloric acid gas in water, determined by the same: —

(5) $\mathbb{HCl} + Aq = (HCl + Aq)$ evolves 17,300^c.

Sixth. The heat developed by burning hydrogen gas in oxygen and condensing the vapor formed, — from the mean of the results of several experimenters: —

(6) $2\,\mathbb{H}_2 + \mathbb{O}_2 = 2\,H_2O$ evolves 138,000^c.

Seventh. The heat developed on dissolving sulphuric oxide in water, determined by Berthelot: —

(7) $SO_3 + H_2O + Aq = (H_2SO_4 + Aq)$ evolves 37,400^c.

Lastly. The heat developed on mixing H_2SO_4 with a large amount of water, determined by several investigators: —

(8) $H_2SO_4 + Aq = (H_2SO_4 + Aq)$ evolves 17,000^c.

If now we analyze reaction (3), it will appear that the heat developed comes not only from the oxidation of the sulphurous acid, but also from the union of chlorine with hydrogen, and, moreover, that the total result is less than the sum of the effects due to these two causes by the amount of heat absorbed in the

* The student should compare this mode of stating the result with that adopted in the table of § 66. The initial letter of the word *calor* placed as above is the usual mode of designating units of heat, and gramme units can be distinguished from kilogramme units by the type as $1{,}000^c = 1^C$.

decomposition of that molecule of water, which yields its oxygen to oxidize the sulphurous acid and its hydrogen to unite with chlorine. Hence the heat developed in the oxidation of sulphurous acid is, by (3), (6), (4), and (5),

$$(H_2SO_3 + Aq) + O = (H_2SO_4 + Aq)$$
$$73{,}900 + 69{,}000 - (44{,}000 + 34{,}600) = 64{,}300^c.$$

Then, by (2),

$$SO_2 + H_2O + O + Aq = (H_2SO_4 + Aq)$$
$$64{,}300 + 7{,}700 = 72{,}000^c.$$

By (1),

$$S + O_2 + H_2O + Aq = (H_2SO_4 + Aq)$$
$$72{,}000 + 69{,}000 = 141{,}000^c.$$

By (7),

$$S + O_3 = SO_3$$
$$141{,}000 - 37{,}400 = 103{,}600^c.$$

By (7) and (8),

$$S + O_3 + H_2O = H_2SO_4$$
$$103{,}600 + 37{,}400 - 17{,}000 = 124{,}000^c.$$

Finally, by (6),

$$S + O_4 + H_2 = H_2SO_4$$
$$124{,}000 + 69{,}000 = 193{,}000^c.$$

It must not be inferred, from the manner in which the result is stated, that we have here reached the heat of combination of the ultimate atoms, for, however desirable such a result would be, it is as yet unattainable. All that we intend to express is that 32 grammes of solid *sulphur*, 64 grammes of *oxygen gas*, and 2 grammes of *hydrogen gas*, when united to form sulphuric acid, H_2SO_4, evolve sufficient heat to raise the temperature of 193,000 grammes of water one degree. Our experiments only prove, it must be noticed, that, in passing from the elementary substances to the ultimate product, through the intermediate stages which the production of sulphuric acid involves, a certain amount of heat is lost on balancing the account. The further conclusion, that the ultimate loss of heat is precisely the same as it would be if sulphuric acid could be made by the direct union of the

elementary substances of which it consists, is an inference from the principles of § 70. In order to determine further the amount of heat evolved in the union of the elementary atoms, starting from a condition in which these atoms are completely dissociated, we must know further the heat of combination of the elementary substances themselves, that is, the heat evolved by the union of the atoms to form the molecules of solid sulphur and of oxygen and hydrogen gases.

A study of the above example will also show that in chemical processes the thermal changes are due not only to chemical action, but also to the change of physical condition which such processes involve. Indeed, on the principle of maximum work (§ 70), the latent heat of an aeriform or liquid product or heat of solution may be the determining cause of a given chemical reaction. Hence it is essential in all studies of this kind to pay the strictest attention to physical conditions, and to state the precise conditions under which a given result was reached. Moreover, it is obvious that, although so simple in theory, the problems of thermo-chemistry may be very complex in practice, and demand a great deal of ingenuity in devising for their solution processes which are compatible with the methods of calorimetry. In order to illustrate these points still further, we add a second example from an investigation of Berthelot.

It was required to determine the heat of formation of aluminic bromide, Al_2Br_6. The heat of formation of aluminic chloride, Al_2Cl_6, had been previously determined by Thomsen, and was known to be 321,800^c. Moreover, the heat of combination of KCl and KBr had been determined by Berthelot, and the heat of solution of these salts was well known. Given these data, Berthelot saw that, if Al_2Cl_6 was dissolved in water containing $6\,KBr$, and, on the other hand, Al_2Br_6 dissolved in the same amount of water containing $6\,KCl$, the final condition of the two solutions must be identical, and hence, by § 70, the total quantity of heat evolved in reaching these conditions, starting from the same elementary substances, must be equal. If then he determined, as could readily be done, the heat of solution in the two cases just mentioned, he could put equal to each other the sums

which represent the total quantity of heat developed in producing the two solutions, and as in this equation the heat of formation of Al_2Br_6 would be the only unknown quantities, the problem was easily solved. Thus we have

$K_6 + Br_6$ (gas) $+ Aq = (6\ KBr + Aq)$	570,000^c
Al_2Cl_6, when dissolved in the previous solution, yielded in the determination of Berthelot,	152,000^c
$Al_2 + Cl_6 = Al_2Cl_6$	321,800^c
	1,043,800^c

On the other hand,

$K_6 + Cl_6 + Aq = (6\ KCl + Aq)$	604,800^c
Al_2Br_6, when dissolved in last solution,	173,800^c
$Al_2 + Br_6 = Al_2Br_6$	x
	778,600$^c + x$

$$x + 778{,}600^c = 1{,}043{,}800^c$$
$$x = 265{,}200^c$$

73. **Results.** — We give in Table V. some of the more interesting results which have thus far been reached in the investigations of thermo-chemistry. They have been for the most part selected from the far more extended tables which have been published in the "Annuaire du Bureau des Longitudes de Paris" since the year 1877.* In a few cases only we have substituted for the numbers in the original table the results of more recent determinations. In order to condense the table, the last two figures of the results as usually given are omitted, and the figures before the decimal point stand for thousands of heat units, as above defined, or for heat units as defined in § 13. The full figures can be obtained by referring to the original papers, but as a rule they are of no value beyond those given in the table. The form of statement adopted in the table has already been fully explained in the last section, and the student must be very careful not to mistake the conventional meaning of the symbols as here used. It is assumed that the constituents are in the condition in which they naturally exist at the temperature of 15° C. and under a pressure of 76 c. m., and the results are based

* Also, Jahresbericht über die Fortschritte der Chemie, 1877.

on experiments made at approximately the same temperature, except in the few cases where it was obviously otherwise. The condition of the product is indicated by the heading of the column in which the figures relating to it are placed. By the heading "Solution" is meant aqueous solution, and the quantity of solvent is assumed to be sufficiently large to determine the maximum thermal effect. Of course, the "Heat of Solution" can be found in any case by subtracting from the numbers of this column the corresponding number in one of the three preceding columns. But it must be noticed that, as thus used, heat of solution is often a mixed effect of simple solution and chemical action; as, for example, when sulphuric oxide or phosphoric oxide is dissolved in water. In a similar way, many other data may be derived from the table which are not explicitly given, and to some of these the student's attention will be called by the problems. But in comparing thermo-chemical data derived from different experimental results, he must not expect to find entire accordance. Although these values are undoubtedly as fundamental constants of chemistry as the atomic weights, yet they have not been as yet so fully confirmed or so thoroughly collated as to enable us to present an entirely consistent system. Hence the table here given must be regarded as provisional, and as serving only to illustrate the principles of the subject. In all cases where important conclusions or practical questions are involved, reference should be had to the original papers, where the details of the several determinations are given, and from these it is usually possible to judge how far the results can be trusted.

74. **Exothermous and Endothermous Bodies.** — An inspection of Table V. will show that, although in most cases heat is evolved in the production of a compound from elementary substances, yet there are many cases in which the formation of the compound body is attended by an absorption of heat. Hence a division of chemical compounds into *exothermous* and *endothermous*; and these two classes are indicated in our table by the plus or minus sign, which is invariably placed before the number of units of heat developed or absorbed. It is obvious that

all endothermous bodies must be more or less unstable, since, according to the principle of maximum work, they must constantly tend to break up into the elementary substances of which they consist. The most remarkable compound of this class on our list is chloride of nitrogen, whose extreme explosive character is well known; and this corresponds to the fact indicated by Table V., that, when nitrogen chloride is resolved into chlorine and nitrogen gases, 38,100 units of heat are set free. The remarkable fact thus brought into prominence might seem at first sight inconsistent with the general principle already enunciated, that, while the union of atoms is attended with the development of heat, the parting of atoms involves a corresponding absorption. But it will be noticed that in the reaction

$$2\,NCl_3 = N{\equiv}N + 3\,Cl\text{-}Cl$$

the nitrogen atoms unite with each other to form molecules of nitrogen gas, and the chlorine atoms in a similar manner to form molecules of chlorine gas, and the amount of heat evolved by the union of these similar atoms so far exceeds the loss of heat which attends the separation of the dissimilar atoms of chlorine and nitrogen, that the difference amounts to over 38,000 units. The peculiar properties of all endothermous compounds are probably to be explained in a similar way, and by studying the thermal relations of such substances we may hope to be able hereafter to determine the heat of combination of the elementary substances themselves, a factor in thermo-chemistry which is greatly wanting to the completeness of this subject. It does not, however, appear that the amount of heat absorbed in the formation of endothermous compounds is the sole measure of their instability, since their molecular structure must have an important influence in this respect; and it is probably due to some circumstance of atomic grouping that acetylene, for example, is so much more stable than chloride of nitrogen, although the heat absorbed in the formation of the molecule C_2H_2 is nearly twice as great as in the production of the molecule NCl_3.

75. **Explosive Agents.** — There are many substances which, although exothermous in respect to the elementary substances

from which they are ultimately derived, are endothermous in their relations to certain definite products into which they are more or less readily resolved with evolution of heat. The ordinary explosive agents are bodies of this class, which owe their efficiency not only to the heat evolved in their decomposition, but also to the circumstance that the products into which they fall are for the most part aeriform bodies, whose molecules acquire an enormous moving power under the influence of the heat thus generated. One of the most remarkable of these substances is nitroglycerine, a frightfully explosive oil, which we may regard as the nitrate of the radical glyceryl $C_3H_5^{'''}O_3^{'''}(NO_2)_3$; and by developing this symbol into the graphic form, the student will see that, although the material contains sufficient oxygen to convert all its carbon into carbonic dioxide and all its hydrogen into water, the greater part of the oxygen atoms are kept apart from the atoms of these very combustible elements by the intervention of atoms of nitrogen in the structure of the molecule. The shock of an exploding fuse is sufficient, however, to disturb the delicate balance of forces by which the unstable structure is maintained, and then the nitroglycerine breaks up, as the following equation* indicates: —

$$C_3H_5N_3O_9 = 3\,CO_2 + 2\tfrac{1}{2}\,H_2O + 1\tfrac{1}{2}\,N_2 + \tfrac{1}{4}\,O_2$$

The great rending effects of the explosion are direct manifestations of the enormous moving power which the molecules of the aeriform products acquire under the influence of the heat developed in the chemical change. Berthelot has determined that the heat of formation of nitroglycerine is 25,000 units. Hence, assuming that the products are cooled down to 15° C., and expanded until reduced in tension to 76 c. m., the heat developed by the explosion must be

$$\begin{array}{cccccc} 3\,\mathfrak{C}\mathfrak{O}_2 & & 2\tfrac{1}{2}\,\mathfrak{H}_2\mathfrak{O} & & C_3H_5N_3O_9 & \\ 282{,}000 & + & 148{,}500 & - & 25{,}000 & = 405{,}500 \text{ units,} \end{array}$$

or 1,786 units for each gramme of the explosive. When it is remembered that this amount of heat is the equivalent of 755.5

* The equation is written conventionally in this form, to avoid large numbers in calculation.

kilogramme metres, and corresponds to a velocity of about 4,000 metres a second imparted to the molecules of that gramme of matter, we find an adequate cause for the effects observed. Moreover, since, when exploded by a fuse, the chemical change takes place, essentially, instantaneously throughout the whole mass of the nitroglycerine, the molecules of the aeriform products, before they have time to expand, strike against the opposing obstacle with the full force of their acquired velocity, and thus a small charge is able to rend a large mass of rock on which it simply rests without any other tamping than the atmospheric air. Another mode of estimating the explosive force is to calculate the temperature of the products by the principles of § 67, and then, assuming that the whole mass of gas is momentarily confined to the space previously occupied by the liquid explosive, determine by [10] and [4] the initial tension. As we know, however, that the laws governing gas tension which these formulas express, do not hold rigorously at the high temperatures and pressures with which we are here dealing, we cannot place much confidence in the results of such calculations.

Although gunpowder is a mechanical mixture, and not a definite compound, the theory of its action is essentially the same as that of nitroglycerine, the chief difference being that, in burning, the chemical action takes place between heterogeneous grains instead of between different parts of the same molecule, and for that reason is less rapid and can be more readily controlled. In both cases the efficiency of the explosive depends upon the circumstance that the aeriform products of the chemical change, confined in a small space and intensely heated, acquire an enormous tension; but while with nitroglycerine all the products are gases, with gunpowder more than one half are solid, and moreover the amount of heat developed in the explosion of nitroglycerine is two and a half times greater than that evolved by the burning of an equal weight of gunpowder.

The composition of gunpowder does not usually vary more than a few per cent from that indicated by the symbols,

$$2\,KNO_3 + S + 3\,C$$

which correspond to 74.9% of nitre, 13.3% of charcoal, and 11.8% of sulphur. These ingredients having been intimately mixed in the condition of fine powder, the resulting meal, moistened with water, is compacted by hydraulic pressure into a solid cake, and this is then broken up by simple mechanical means into grains of different sizes. The following facts in regard to the burning of gunpowder in closed vessels are the results of a very able investigation of the subject made by Abel and Noble.

When one gramme of powder is burnt, the solid products amount to about 0.57 gramme, and the aeriform products to about 0.43 gramme. The solid products are chiefly a mixture of potassic carbonate, sulphate, thiosulphite, and sulphide, with remnants of unburnt powder in very varying proportions. The composition of the aeriform product is more constant, and does not vary much from 50% CO_2, 11% CO, 34% N_2, 3% H_2S, 2% H_2. The volume of gas furnished by the combustion of one gramme of powder in a closed vessel measured at 0° and 76 c. m. is about 280 $\overline{\text{c. m.}}^3$, and is about 280 times the volume of the gunpowder, whose density does not vary greatly from that of water. The tension of the products of combustion, when the powder entirely fills the space in which it is fired, is about 6,400 atmospheres, or 42 tons per square inch. The heat developed by the burning of one gramme of powder is about 705 gramme units, and the temperature momentarily developed about 2,200° C. The total work of gunpowder when the products are indefinitely expanded is theoretically about 332,000 metre grammes per gramme, or 480 foot tons per pound of powder.

76. **Chemical Affinity.** — The force which holds together the atoms in a molecule is usually called chemical affinity, and chemical changes are frequently ascribed to the different affinities for each other which different atoms possess. In the older works on chemistry great stress was laid on what were called the elective affinities of substances, compounds as well as elements; and Bergman, a celebrated chemist of the last century, published a series of tables which were supposed to give the relative affinities of the more important chemical agents known in his time, as indicated chiefly by the order in which they would replace each

other in a series of chemical reactions. Thus we have the relative affinities of sulphuric acid for different bases, and, on the other hand, the relative affinities of a base like potash for the different acids. The word *affinity* originated in the conception of some affection inherent in a body, by virtue of which it combined with one substance in preference to another, and, like many other scientific terms, has long survived its original meaning. In regard to the nature of the chemical force (affinity), there have been many different opinions among natural philosophers. Some, like Newton and Berthollet, have regarded it as a phase of universal attraction; others, like Davy and Berzelius, have considered it to be a manifestation of electrical action; while many students of the present day are inclined to regard all chemical change as an effect of the motions of atoms. But although we have not been able to attain any clearer views of the essential nature of the chemical force than such a diversity of opinions would indicate, yet in the principle of maximum work we have obtained from the study of thermo-chemistry a very important generalization, which enables us in most cases to predict the result of a given combination of materials and conditions. Thus, to add another example to those already given, we are enabled to predict, from the data given in Table V., that, when bits of metallic zinc are placed in sulphuric acid diluted with water, a chemical reaction will take place by which hydrogen gas and a solution of zinc sulphate will be formed.

If now we examine closely the details of this very simple thermo-chemical problem, we shall find that the changes of physical condition are the chief causes which determine the chemical change. The formation of sulphuric acid from hydrogen gas, which our calculation assumes, implies the expenditure of a large amount of work in changing an aeriform to a liquid condition, and hence the hydrogen atoms while in combination may be regarded as having a certain energy of position, which facilitates their return to the condition of gas. Then, again, the solution of the zinc sulphate is another important element in the process; for, as is well known, all chemical action ceases as soon as the water becomes saturated, although a large excess both of sulphuric acid and zinc may be present.

But after making all allowances for the potency of physical conditions, it would appear, from the present standpoint of chemistry, that there must be certain differences of qualities inherent in the atoms, which correspond to what we call differences of chemical affinity, and which are important factors in determining chemical changes; and it is certainly legitimate to seek to measure what we may call the relative *potential* of the atoms when in a state of indefinite expansion.*

77. **Thermolysis, or Dissociation.**—The heat which is evolved in most cases when elementary substances unite to form compounds, represents a certain amount of work which the chemical process accomplishes, and we should therefore expect from analogy that heat would be able to undo this same work, and hence that at a sufficiently high temperature the compound would be again resolved into elements. Thus, when one gramme of hydrogen gas unites with eight grammes of oxygen gas to form water, 34½ kilogramme units of heat are evolved, which are the equivalent of 14,600 kilogramme metres of work, and the gases in combining have lost that peculiar movement of their atoms and molecules which was the essential condition of their previous state. Now it is just this quantity of motion which in the act of combination is converted into heat, and it is to be expected that, if the same amount of motion is restored under the influence of a high temperature, the water will be converted back into the elementary gases. Such we find to be actually the case. According to Deville, when steam is passed through a heated platinum tube, decomposition commences at from 960° to 1,000°; but it is not completed until a much higher temperature is reached. Under these conditions a small part of the hydrogen gas escapes by a kind of osmotic action through the walls of the platinum tube, but the rest recombines with the oxygen when the vapor cools, leaving, however, a volume of oxygen half as great as that of the escaped hydrogen, which can be collected and measured. With a tube of the very costly metal palladium, the osmotic action is so strong under the same circumstances as to deter-

* The student will find a notice of a partial solution of this problem by Thomsen, in the American Journal of Science, Vol. XXI., February, 1881.

mine a very considerable separation of the two gases; and a similar, although less perfect separation can be obtained with a tube of porous earthen-ware, from which hydrogen escapes by diffusion.

In many cases when a compound is decomposed by heat, the constituents do not recombine when the temperature falls. We should expect such a result in the case of endothermous bodies like the oxides of nitrogen, but the same is true of many exothermous substances. Thus, when passed through a red-hot tube, ammonia gas is permanently resolved into a mixture of hydrogen and nitrogen gases, hydric sulphide into hydrogen gas and sulphur vapor, marsh gas into hydrogen gas and coke; and, indeed, almost all compounds, both of carbon and of nitrogen, are permanently decomposed at a red heat.

The term *thermolysis*, corresponding to *electrolysis*, very accurately describes phenomena of this class, and is to be preferred to the word *dissociation*, which is less significant. By some authors the last term is reserved for those cases of thermolysis in which the elementary substances would recombine if the temperature fell to a sufficient degree, and it is convenient to speak of the elements when in this state as dissociated. If we can rely on the evidence of the spectroscope, all the present elements become dissociated at temperatures which we can readily command. The greater part of the metallic salts are thermolyzed in the flame of a Bunsen burner, and no known compound resists the high temperature which is obtained by the discharge of a powerful induction coil when intensified by a Leyden jar. Indeed, there is reason to believe that under these circumstances some of the substances hitherto regarded as elementary are temporarily resolved into simpler conditions. Moreover, the spectroscope indicates that on the surface of the sun the chemical elements are actually in a state of permanent dissociation, if not in some cases themselves decomposed. According to the nebular theory our earth must have passed through a similar stage, and not until the crust had cooled could chemical combination begin; and in imagination we can go back to a still earlier period, when there was but one *substance*, and regard all chemical qualities and

relations as the results of the successive differentiations of this primeval mass as it gradually cooled.

The principles of this section have a very important bearing on the determination of molecular weights by means of vapor densities (§ 18); for it is evident that, if in the process the vapor undergoes thermolysis, the result must be wholly vitiated. In some cases dissociation follows volatilization so immediately that the abnormal vapor density is the only direct evidence we have of the decomposition. For example, the density of the vapor of ammonic chloride, instead of being 26.75, as we should expect from the undoubted weight of its molecule, NH_4Cl, is only about one half of this amount; and the reason probably is, that, when heated, the molecule breaks into two, and, in consequence, the volume of the vapor doubles.

$$\boxed{NH_4Cl} = \boxed{NH_3} + \boxed{HCl}$$

So, also, chloral hydrate yields a vapor density which is only half as great as the admitted constitution of its molecule demands; and although it is to a high degree probable that this compound would break up, when heated, into chloral and water, yet it is very difficult to obtain any convincing evidence that such a change has taken place. In both the cases we have cited the molecules recombine in assuming the solid condition, and all the phenomena attending the change of state are precisely the same as those observed in any other volatile body. Indeed, although many very ingenious experiments have been made with a view of settling the question, it is still uncertain, not only in this, but also in several other cases, whether dissociation has taken place or not. The question is of great importance to the theory of chemistry. If dissociation does not take place, the cases referred to are exceptions to the law of equal molecular volumes, and specific gravity can no longer be regarded, as now, the sole measure of molecular weight. If, however, it can be proved that such a change does take place, then the unity of our present theory is preserved, and the

chemist has only to guard against this cause of error in his experiments.

When dissociation does not begin until the temperature has risen considerably above the point at which the substance becomes a permanent gas, the change is marked by a more or less rapid falling off of the vapor density as the temperature rises. Such a change can be discovered by repeating the observation at different temperatures, and it is only when the values thus obtained are constant, that entire reliance can be placed upon the observation. The gradual change of density, which is the indication of dissociation under such circumstances, is strikingly illustrated by the vapor of sulphur. The vapor density of this elementary substance at temperatures near its boiling-point is, according to Deville, 6.62 (referred to air), which corresponds very closely to the theoretical density for S_6. Above 500° the density gradually diminishes, but becomes constant again at about 800°, and above this the density is 2.23, which corresponds to the symbol S_2. A still more striking illustration of the same principle is furnished by the recent experiments of Crafts and Meier on the density of iodine vapor at high temperatures and low tensions. Through quite a wide variation of temperature, between 350° and 700°, the density of the vapor is 8.8, which corresponds closely to the theoretical density for $I\text{-}I$ where $I = 127$. But above 700° the density gradually diminishes, and at 1,500° again becomes constant at 4.6, which is nearly the theoretical density a gas would have whose molecules were isolated atoms of iodine.

Victor and Carl Meyer in their experiments, at high temperatures, on the density of chlorine gas, as well as iodine vapor, only succeeded in reducing the density in either case to two thirds of the normal values. But they experimented at the tension of the air, while Crafts and Meier worked with a mixture of air and iodine vapor, in which the tension of the vapor was comparatively small, and this circumstance fully explains the difference in the results. Not only does a low tension favor dissociation, but, as Regnault has shown, the lower the tension the more nearly do aeriform substances obey the law of Mariotte, and therefore the more closely will the observed density agree with the theoretical value (§ 18).

A change of vapor density similar to that just described is sometimes observed near the boiling-point of a volatile substance. This is well shown by a series of determinations of the specific gravity of the vapor of acetic acid made by Cahours. This acid, when in the most concentrated state, boils at 120°, and the specific gravity of its vapor referred to hydrogen at the same temperature and pressure was found to have the following values at the temperatures indicated: —

At 125°	45.90	At 170°	35.30	At 240°	30.16
" 130	44.82	" 180	35.19	" 270	30.14
" 140	41.96	" 190	34.33	" 310	30.10
" 150	39.37	" 200	32.44	" 320	30.07
" 160	37.59	" 220	30.77	" 336	30.07

It will be noticed that, as the temperature increases, the specific gravity diminishes, at first very rapidly, afterwards more slowly, and does not become constant until the temperature has risen 125° above the boiling-point, when we have the true specific gravity of acetic acid in the state of gas. This gives for the molecular weight of acetic acid 60 very nearly, which corresponds to the received formula, $C_2H_4O_2$. The variations in such cases are to be referred to the same causes which determine even in the permanent gases slight deviations from Mariotte's law, and the normal density is not reached until the molecules are so far separated as to render their attraction for each other insensible. It is only when in this condition, the condition of a true gas, that equal volumes of all substances contain the same number of molecules; and while some substances, like water and alcohol, assume this state at temperatures only a few degrees above their boiling-point, other substances must be heated to a much higher temperature before the effect of molecular attraction in increasing the density of the vapor ceases to be felt. Evidently the action of heat in overcoming molecular attraction is an effect of the same class as dissociation, and the two phenomena we have been considering are closely allied.

In deducing molecular weights from vapor densities we must

be on our guard against both of these sources of error, and it is only when the specific gravity remains constant under varying temperature that we can deduce any safe conclusions from the results obtained.

QUESTIONS AND PROBLEMS.

1. How many times more space does the carbonic dioxide formed by burning charcoal (*Sp. Gr.* = 2) occupy than the charcoal burnt?

Ans. 1 cubic centimetre (or 2 grammes) of charcoal yields 3.720 litres. Hence the gas occupies 3,720 times the volume of the charcoal.

2. How many litres of oxygen gas are required to burn 1 litre of alcohol vapor, and how many litres of aqueous vapor, and how many of carbonic dioxide, will be formed in the process?

Ans. 3 litres of oxygen, 3 litres of aqueous vapor, 2 litres of carbonic dioxide.

3. Given the symbol of alcohol, C_2H_6O, to find its calorific power.

Ans. 6,572 units, or 7,200 units, assuming that the steam formed was condensed.

4. The composition of dried peat is as follows: Carbon, 625.4; Hydrogen, 68.1; Oxygen, 292.4; Nitrogen, 14.1. Find the calorific power. Ans. 5,811 units.

5. Find the calorific intensity of marsh gas burnt in oxygen.

$$CH_4 + 2\,O{=}O = CO_2 + 2\,H_2O$$

Calorific power of marsh gas, 13,063. Specific heat of steam, 0.4805; of CO_2, 0.2164. Ans. 7,793°.

6. Find the calorific intensity of olefiant gas burnt in oxygen.

$$C_2H_4 + 3\,O{=}O = 2\,CO_2 + 2\,H_2O$$

Calorific power of C_2H_4, 11,858. Specific heat of steam and carbonic dioxide as in last problem. Ans. 9,136°.

7. Find the calorific intensity of marsh gas and olefiant gas burnt in air. Besides the data already given, we have also specific heat of nitrogen, 0.244. Ans. 2,662° and 2,916°.

8. Determine the heat of combination of $H + Br = HBr$ from the following data: —

$$(KBr + Aq) + \tfrac{1}{2}\,Cl_2 = (KCl + \tfrac{1}{2}\,Br_2 + Aq) \quad 11{,}478^c$$

$$\tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,Cl_2 + Aq = (HCl + Aq) \quad 39{,}315^c$$

$$(KOH + Aq) + (HCl + Aq) = (KCl + Aq) \quad 13{,}750^c$$

$$(KOH + Aq) + (HBr + Aq) = (KBr + Aq) \quad 13{,}750^c$$

$$\tfrac{1}{2}\,Br_2 + Aq = (\tfrac{1}{2}\,Br_2 + Aq) \quad 539^c$$

$$HBr + Aq = (HBr + Aq) \quad 19{,}940^c$$

Ans. 8,436c.

9. Determine the heat of combination of $H + I = HI$ from the following data, in addition to those given in the last problem: —

$$(KOH + Aq) + (HI + Aq) = (KI + Aq) \quad 13{,}680^c$$

$$(KI + Aq) + \tfrac{1}{2}\,Cl_2 = (KCl + Aq) + \tfrac{1}{2}\,I_2 \quad 26{,}209^c$$

$$HI + Aq = (HI + Aq) \quad 19{,}210^c$$

Ans. —6,034c.

10. Determine the heat of combination of $N + H_3 = NH_3$ from the following data, in addition to those given in Problem 8: —

$$(\tfrac{1}{3}\,NH_3 + Aq) + \tfrac{1}{3}\,Cl_2 = (NH_4Cl + Aq) + \tfrac{1}{6}\,N_2 \quad 39{,}871^c$$

$$(HCl + Aq) + (NH_3 + Aq) = (NH_4Cl + Aq) \quad 12{,}270^c$$

$$NH_3 + Aq = (NH_3 + Aq) \quad 8{,}435^c$$

Ans. 26,707c.

11. Determine the heat of combination of $H_2 + S = H_2S$ from the following data, in addition to those given in Problem 9: —

$$(I_2 + Aq) + H_2S = (2\,HI + Aq) + \tfrac{1}{2}\,S_2 \quad 21{,}830^c$$

Ans. 4,522c.

12. Determine the heat of combination of $C + H_4 = CH_4$, $C_2 + H_4 = C_2H_4$, and $C_2 + H_2 = C_2H_2$, knowing that the heat of combustion of these typical hydrocarbons is as follows: —

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O \qquad 210{,}000^c$$
$$C_2H_4 + 3\,O_2 = 2\,CO_2 + 2\,H_2O \qquad 334{,}000^c$$
$$C_2H_2 + \tfrac{5}{2}\,O_2 = 2\,CO_2 + H_2O \qquad 321{,}000^c$$

Ans. CH_4, $+22{,}000^c$; C_2H_4, $-8{,}000^c$; C_2H_2, $-64{,}000^c$.

13. Calculate from the data given in Table V. the amount of heat evolved in the two following reactions: —

$$KClO_3 = KCl + \tfrac{3}{2}\,O_2$$
$$NH_4NO_3 = 2\,H_2O \text{ (liquid)} + N_2O$$

14. Analyze the following reaction, and show that it corresponds to the principle of maximum work: —

$$Zn + (H_2SO_4 + Aq) = (ZnSO_4 + Aq) + H_2$$

Why is not a corresponding reaction possible with copper?

15. Assuming that the symbol of gun-cotton is $C_{12}H_{15}N_5O_{20}$, and that the heat of formation is 502,000 units, calculate the amount of heat developed by the explosion of one gramme. To how many kilogramme metres does the heat thus generated correspond, and what velocity does it impart to the products of the explosion?

16. At the temperature of 470° the Sp. Gr. of the vapor of sulphuric acid is approximately 1.697. How does this result agree with the generally received symbol of this compound, and how do you explain the discrepancy?

CHAPTER XIV.

RELATIONS OF THE ATOMS TO LIGHT.

78. **Light a Mode of Atomic Motion.** — It has already been intimated (§ 66, note), that the phenomena of vision are the effects of an atomic motion transmitted from some luminous body to the eye through continuous lines of material particles, and such lines we call rays of light. This motion may originate with the atoms of *various* substances; but in order to explain its transmission, we are obliged to assume the existence of a medium filling all space, of extreme tenuity, and yet having an elasticity sufficiently great to transmit the luminous pulsations with the incredible velocity of 186,380 miles in a second of time. This medium we call the ether, but of its existence we have no definite knowledge except that obtained through the phenomena of light themselves, and these require assumptions in regard to the constitution of the ethereal medium which are not realized even approximately in the ordinary forms of matter; for while the assumed medium must be vastly less dense than hydrogen, its elasticity must surpass that of steel, and be of the same kind.

According to the undulatory theory, motion is transmitted from particle to particle along the line of each luminous wave, very much in the same way that it passes along the line of ivory balls in the well-known experiment of mechanics. The ethereal atoms are thus thrown into waves, and the order of the phenomena is similar to that with which all are familiar in the grosser forms of wave motion. But in this connection we have no occasion to dwell on the mechanical conditions attending the transmission of the motion. The motion itself may be best conceived as an oscillation of each ether particle in a plane perpendicular to the direction of the ray, not necessarily, how-

ever, in a straight line; for the orbit of the oscillating molecule may be either a straight line, an ellipse, or a circle, as the case may be. Such oscillations may evidently differ both as regards their amplitude and their duration, and on these fundamental elements depend two important differences in the effect of the motion on the organs of vision; namely, intensity and quality, or brilliancy and color.

If our theory is correct, it is obvious that the intensity of the luminous impression must depend upon the force of the atomic blows which are transmitted to the optic nerves, and it is also evident that this force must be proportional to the square of the velocity of the oscillating atoms, or, what amounts to the same thing, to the square of the amplitude of the oscillation; assuming, of course, that the oscillations are isochronous.

The connection of color with the time of oscillation is not so obvious, and why it is that the waves of ether beating with greater or less rapidity on the retina should produce such sensations as those of violet, blue, yellow, or red, the physiologist is wholly unable to explain. We have, however, an analogous phenomenon in sound, for musical notes are simply the effects of waves of air beating in a similar way on the auditory nerves; and, as is well known, the greater the frequency of the beats, or, in other words, the more rapid the oscillations of the aerial molecules, the higher is the pitch of the note. Red color corresponds to low, and violet to high notes of music, and the gradations of color between these extremes, passing through various shades of yellow, green, blue, and indigo, correspond to the well-known gradations of musical pitch.

By well-known means we can measure the lengths of the ether waves, and from these data we can easily calculate the rapidity of the oscillations which produce the different sensations of color. The following table contains the results. It must be understood, however, that these numbers merely correspond to a few shades of color definitely marked on the solar spectrum by certain very prominent dark lines hereafter to be mentioned, which are designated by the letters of the alphabet; and that equally definite values may be assigned to the infinite number

of intermediate shades which intervene between these arbitrary subdivisions of the chromatic scale.

WAVES OF LIGHT.

Wave Lengths adopted by Angström.

Color.		Length of Waves in 10^{-10} of a Metre.	Number of Waves or Oscillations in one Second.
Red	*A*	7604.00	394,350 thousand million.
	B	6867.00	436,674 " "
	C	6562.01	456,970 " "
Yellow	*D*	5892.12	508,924 " "
Green	*E*	5269.13	569,096 " "
Blue	*F*	4860.72	616,913 " "
Indigo	*G*	4307.25	696,184 " "
Violet	H_1	3968.01	755,704 " "
	H_2	3933.00	762,431 " "

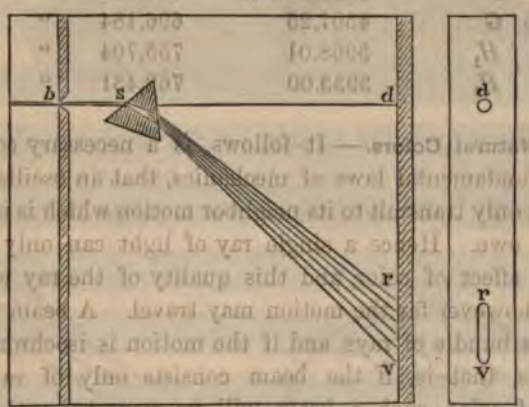
79. **Natural Colors.** — It follows, as a necessary consequence of the fundamental laws of mechanics, that an oscillating molecule can only transmit to its neighbor motion which is isochronous with its own. Hence a single ray of light can only produce a definite effect of color, and this quality of the ray will be preserved, however far the motion may travel. A beam of light is simply a bundle of rays, and if the motion is isochronous in all its parts, that is, if the beam consists only of rays of one shade of color, such a beam will be *monochromatic*, and will produce the simplest chromatic sensation possible, — that of a simple color. If, however, the beam contains rays of different colors, we shall have a more complex effect, and the infinite variety of natural tints are thus produced. When, lastly, the beam contains rays of all the colors mingled in due proportion, we receive an impression in which no single color predominates, and this we call white light.

The colors of natural objects, whether inherent or imparted by various dyes, are simply effects upon the retina produced by the beam after it has been reflected from the surface or transmitted through the mass of the body, and the peculiar chromatic effects are due to the unequal proportions in which the different colored

rays are thus absorbed. The color reflected, and that absorbed or transmitted, are always complementary to each other, and if mingled they would reproduce white. It is obvious, moreover, that no beam of light, however modified by reflection or transmission, could produce the sensation of a given color if it did not contain from the first the corresponding colored rays. Hence it is that the colors of objects only appear natural by daylight; and when illuminated by a monochromatic light, all colors blend in that of this one pure tint.

80. **Chromatic Spectra and Spectroscopes.** — When a beam of light is passed through a glass prism placed as shown in Fig. 4,

Fig. 4.



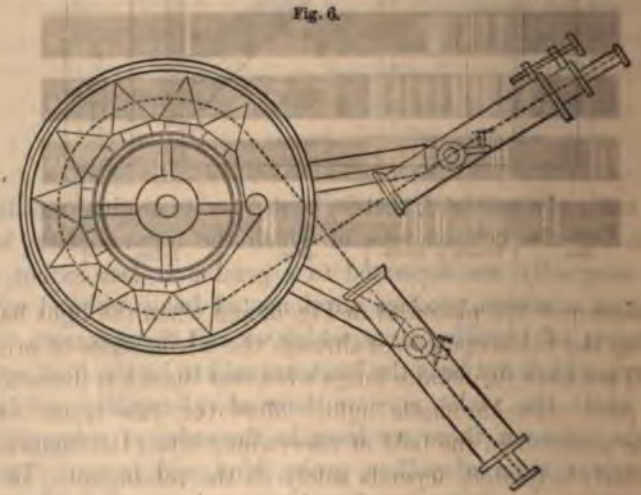
it is not only *refracted*, that is, bent from its original rectilinear course, but the colored rays of which the beam consists, being bent unequally, are separated to a greater or less extent, and, falling on a screen, produce an elongated image colored with a succession of blending tints, which we call the spectrum. The red rays, which are bent the least, are said to be the *least refrangible*, while the violet rays are the *most refrangible*; and intermediate between these we have, in the order of refrangibility, the various tints of yellow, green, blue, and indigo. Thus a prism gives an easy means of analyzing a beam of light, and of discovering the character of the rays by which a given chromatic effect is produced. Such observations are very greatly facilitated

by a class of instruments called spectroscopes, and Figs. 5 and 8 will illustrate the principles of their construction.

Fig. 5.

In the very powerful instrument first represented, the beam of light is passed in succession through nine prisms (each having an angle of 45°), and the extreme rays are thus widely separated,

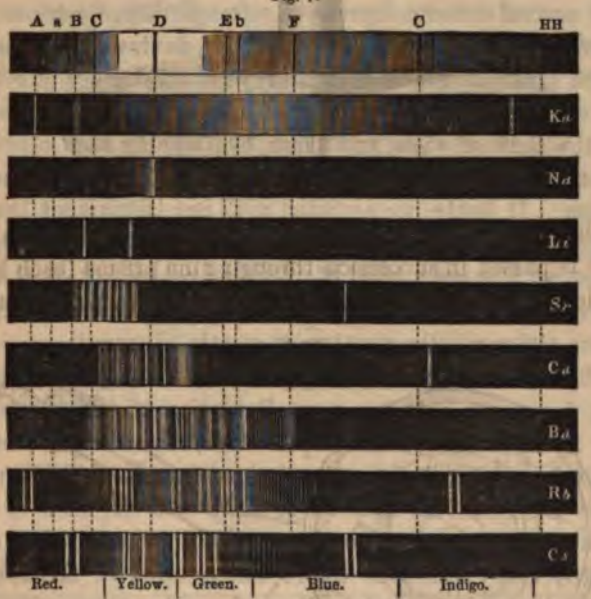
Fig. 6.



while the beam itself is bent around nearly a whole circumference. The only other essential parts of the instrument are the

collimator A and the telescope B. The light first enters the collimator through a narrow slit, and, having passed through the prisms, is received by the telescope. The telescope is adjusted as it would be for viewing distant objects, and a lens at the end of the collimator serves to render the rays diverging from the slit parallel, so that, when the two tubes are in line, one sees through the telescope a magnified image of the slit, just as if the slit were at a great distance. In like manner, when

Fig. 7.



the telescopes are placed as in Fig. 6, and when the light before reaching the telescope passes through the whole series of prisms, we still see a single definite image whenever the slit is illuminated by a pure monochromatic light. Moreover, this image has a definite position in the field of view, which, when the instrument is similarly adjusted, depends solely on the refrangibility of the light.

Thus, if we place in front of the slit a sodium flame, which emits a pure yellow light, we see a single yellow image of this

longitudinal opening, as in Fig. 7, *Na*. If we use a lithium flame, we see a similar image,* but colored red, and at some distance from the first, to the left, if the parts of our instrument are disposed as in Fig. 8. If we use a thallium flame, we in like manner see a single image, but colored green, and falling considerably to the right of both of the other two. If now we illuminate the slit by the three flames simultaneously, we see all three images at once in the same relative position as before. So also, if we examine the flame of a metal, which emits rays of several definite degrees of refrangibility, we see an equal number of definite images of the slit. If, next, we illuminate the slit with sunlight, which contains rays of all degrees of refrangibility, we see an infinite number of images of the slit spread out along the field of view, and these, overlapping each other, form that continuous band of blending colors which we call the solar spectrum. If, lastly, we examine with our instrument the light reflected from a colored surface, or transmitted through a colored medium, we also see a band of blending colors, but at the same time we observe that certain portions of the normal solar spectrum are either wholly wanting or greatly obscured.

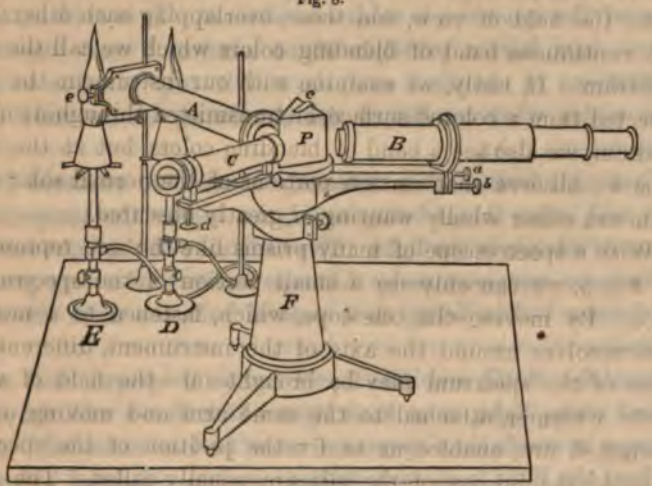
With a spectroscope of many prisms like the one represented by Fig. 5, we can only see a small portion of the spectrum at once. By moving the telescope, which, fastened to a metallic arm, revolves around the axis of the instrument, different portions of the spectrum may be brought into the field of view; while a vernier, attached to the same arm and moving over a graduated arc, enables us to fix the position of the spectrum lines, as the images of the slit are usually called. The other mechanical details shown in the figure are required in order to adjust the various parts of the instrument, and especially in order to bring the prisms to what is termed the angle of minimum deviation. But an instrument of this magnitude and power is not required for the ordinary applications of the spectroscope in chemistry. For this purpose a small instrument, consisting of a collimator, a single prism, and a telescope, all in a fixed position, is amply sufficient. In the field of such a

* The second image shown in Fig. 7, *Li*, is not ordinarily seen.

spectroscope the whole spectrum may be seen at once; and the position of the spectrum lines is very easily determined by means of a photographic scale placed at one side, and seen by light reflected into the telescope from the face of the prism.

The various parts of the instrument, as arranged for observation, are shown in Fig. 8. *A* is the collimator, *P* the prism, and *B* the telescope. The tube *C* carries the photographic scale, and has at the end nearest to the prism a lens of such focal length that the image both of the slit and the scale may be seen through the telescope at the same time, the one appearing projected upon the other. The screw *e* serves to adjust the width of the slit. Moreover, one half of the length of the slit is

Fig. 8.



covered by a small glass prism, so arranged that it reflects into the collimator tube the rays from a lamp placed on one side. Thus the two halves of the slit may be illuminated independently by light from different sources, and the two spectra, which are then seen superimposed upon each other (see Fig. 9), exactly compared. The various screws, which appear in Fig. 8, are used for adjusting the different parts of the instrument.

81. **Spectrum Analysis.** — The atoms of the different chemical elements, when rendered luminous under certain definite condi-

tions, always emit light whose color is more or less characteristic, and which, when analyzed with the spectroscope, exhibit spectra similar to those which are represented in Fig. 7, so far as is possible without the aid of color. Sometimes we see only a single line in a definite position, as in the case of *Na*, *Li*, and *Tl*, already referred to. At other times there are several such lines; and, still more frequently, to these lines (or definite images of the slit) there are superadded more or less extended portions of a continuous spectrum. Moreover, not only is the general aspect of each spectrum exceedingly characteristic, but the occurrence of its peculiar lines is also, so far as we know, an absolute proof of the presence of a given element, and these lines may be readily recognized by their position, even when the character of the spectrum is otherwise obscure. It is evident, then, that we have here a principle which admits of most important applications in chemical analysis, and it only remains to consider under what conditions the elementary atoms emit their characteristic light.

First. All bodies when intensely heated are rendered luminous, and, other things being equal, the higher the temperature the more intense is the light. The brilliancy of the light emitted at the same temperature by different bodies varies very greatly, the densest bodies being, as a general rule, the most intensely luminous.

Secondly. Solid, and also liquid bodies if opaque, emit when ignited white light, or at least light which shows with the spectroscope a continuous spectrum more or less extended. At a red heat the light from such bodies consists chiefly of red rays, but as the temperature rises first to a white and then to a blue heat, the more refrangible rays become more abundant, and finally predominate.

Thirdly. The elementary substances give out their peculiar and characteristic light only in the state of gas or vapor. Hence, when we examine with a spectroscope a source of light, we may infer that a continuous spectrum indicates the presence of solid or liquid bodies, while a discontinuous spectrum, with definite lines or images of the slit, indicates the presence of gases and

vapors; and in the last case we can, as has been seen, infer from the position of the lines the nature of the luminous atoms. It would seem, however, from recent investigations, that under certain conditions even a gas may show a continuous spectrum, and there are other seeming exceptions which admonish us that the general principles just stated should be applied with caution.

Fourthly. At the very high temperatures at which alone gases or vapors become luminous, compound bodies, as a rule, appear to be decomposed, and the elementary atoms dissociated. Hence the observations with the spectroscope have been almost entirely confined to the spectra of the elementary substances, and our knowledge of the spectra of compound substances is exceedingly limited. In some few cases where the spectrum of a compound has been obtained, it has been noticed that, as the temperature rises, this spectrum is suddenly resolved into the separate spectra of the elements of which the compound consists.

Fifthly. At a high temperature the metallic atoms of a compound body are far more luminous than those of the other elementary atoms with which they are associated. Hence, when the vapor of a metallic compound is rendered luminous, the light emitted is so exclusively that of the metallic atoms, dissociated by the heat, that when examined with the spectroscope the spectrum of the metal is alone seen; and this is the probable explanation of the fact that the salts of the same metal, when treated as will be described in the next paragraph, all show, as a general rule, the same spectrum as the metal itself.

Lastly. The substance on which we wish to experiment may be rendered luminous in several ways. If the substance is a volatile metallic salt, the simplest method is to expose a bead of the substance (supported on a loop of platinum wire) to the flame of a Bunsen burner (Fig. 8), which by itself burns with a nearly non-luminous flame. The flame soon becomes filled with the dissociated atoms of the metal, and shines with their peculiar light.

In order to study the spectra of the less volatile metals, like

aluminum, iron, or nickel, we use two needles of the metal, and pass between the points, when about one fourth of an inch apart, the electric discharges of a powerful Ruhmkorff coil, condensed by a large Leyden jar. The metal is volatilized by the heat of the electric current, and the space between the points becomes filled with the intensely ignited vapor, which then shines with its characteristic light.*

In a similar way we can experiment on the permanent gases and lighter vapors, enclosing them in a glass tube with platinum electrodes, and before sealing the tube reducing the tension with an air-pump, when the discharge will pass through a length of several inches of the attenuated gas. The light then emitted comes from the atoms or molecules of the gas, and where the electric current is condensed, as in the capillary portion of the tubes constructed for this purpose, the light is sufficiently intense to be analyzed with the spectroscope.

The three different modes of experimenting just described do not by any means always give the same spectrum when applied to the same chemical element. It constantly happens that as the temperature rises new lines appear, which are usually those corresponding to the more refrangible rays, and at the very high temperatures generated by the electric discharge many of the spectra change their whole aspect. The ill-defined broad bands or luminous spaces which are so conspicuous at a low temperature (see Fig. 7) disappear, and are replaced by a greater or less number of definite spectrum lines. Generally, however, the characteristic lines which mark the element at the lower temperature are seen also at the higher; but sometimes there is a sudden and complete change of the whole spectrum. The cause of these differences is not fully understood, but it has been thought by some investigators that the normal spectra of the elementary atoms consist of bright bands alone, and that the more or less continuous spectra, which are also seen at the lower temperatures, are to be referred to the imperfect dissociation of the atoms, whose mutual attractions or partial combinations produce a state

* An electric spark is in every case merely a line of material particles rendered luminous by the current.

of aggregation approaching the condition which determines the continuous spectra of liquid or solid bodies. Indeed, there is reason to believe that the remarkable transformations which have been observed in the spectra of some of the metals, when their vapors have been rendered luminous by the discharge of a very powerful induction coil, are in fact indications of the dissociation of what we have hitherto regarded as elementary substances.

82. **Delicacy of the Method.** — Having now stated the general principles of spectrum analysis, and the conditions under which these principles may be applied, it need only be added that the method is one of extreme delicacy. It enables us to detect wonderfully minute quantities of many of the metallic elements, and has already led to the discovery of four elements of this class which had eluded all methods of investigation previously employed. The names of these elements, rubidium, cæsium, thallium, and indium, all refer to the color of their most characteristic spectrum bands.*

83. **Solar and Stellar Chemistry.** — When a beam of sunlight is examined with a powerful spectroscope, the solar spectrum is seen to be crossed by an almost countless number of *dark lines*, distributed with no apparent regularity, and differing very greatly in relative strength or intensity. These lines were first accurately described by the German optician, Fraunhofer, and have since been known as the Fraunhofer lines. A few of the most prominent of these lines are shown in Fig. 7, with the letters of the alphabet by which they are designated. These lines, like the bright lines of the elements, correspond in every case to a definite degree of refrangibility, and therefore have fixed positions on the scale of the spectroscope. Moreover, what is very remarkable, these positions are in several cases absolutely the same as those of certain well-known bright lines.

It is easy to construct the spectroscope so that the upper and lower halves of the slit may be illuminated from different sources. If then we admit a beam of sunlight through one half, and the

* The different bands of the same element are usually distinguished by Greek letters, following the order of relative brilliancy.

light of a sodium flame through the other half, we shall have the two spectra superimposed in the same field, as in Fig. 9, and it will be seen that the two parts of the sodium band, which appears as a double line under a high power, coincide absolutely in position with the double dark line D in the solar spectrum. But a still more striking coincidence has been observed in the case of iron, for the eighty well-marked bright lines in the spectrum of this metal correspond absolutely, both in position and in strength, with eighty of the dark lines of the solar spectrum. Now the chances that such coincidences are the result of accident are not one in one billion billion; and we are therefore compelled to believe that the two phenomena must be connected. A simple experiment shows what the relation probably is.

Fig. 9.

If we place before the spectroscope a sodium flame, we see, of course, the familiar double line. If now we place behind the sodium flame a candle flame, so that the candle also shines into the slit, but only through the sodium flame, we shall see the same bright lines projected upon the continuous spectrum of the candle. If, however, we put in place of the candle an electric light, we shall find that, while the continuous spectrum is now far more brilliant than before, the sodium lines appear black. The explanation of this singular phenomenon is to be found in a principle, now well established both theoretically and experimentally, that a mass of luminous vapor, while otherwise transparent, powerfully absorbs rays of the same refrangibility as those which it emits itself. Hence, in our experiment, the very small portion of the spectrum covered by the sodium line is illuminated by the sodium flame alone, while all the rest of the spectrum is illuminated from the source behind, and the

effect is merely one of contrast, the sodium lines appearing light or dark according as they are brighter or darker than the contiguous portions of the spectrum.

In a similar way the bright lines of a few other elements have been inverted, and these experiments would lead us to infer that the Fraunhofer lines themselves are formed by a brilliant photosphere shining through a mass of less luminous gas. In other words, it would appear that the sun's luminous orb is surrounded by an immense atmosphere which intercepts a portion of his rays, and that we see as dark lines what would appear as bright bands could we examine the light from the atmosphere alone. This can readily be done when the sun's luminous disk is covered by the moon at the time of a total eclipse, and then bright bands corresponding to the more prominent dark lines have been seen with great distinctness.

The dark lines of the solar spectrum have been most carefully mapped and compared with the spectra of the known elements, and all the resources of photography have been used to facilitate and insure accuracy in the comparison; and it appears, not only that the lines of many of our supposed terrestrial elements are not found in the solar spectrum, but also that there are a large number of solar lines which, so far as we know, do not correspond to any of the known elements. Still, as new elements are not unfrequently found on the earth, we should not be surprised to find many new forms of elementary matter at the centre of the solar system, and, on the other hand, it is possible that some of our elementary substances may be dissociated at the high temperature of the sun. Indeed, a part of the complexity we see in the solar spectrum may arise from the formation of what we call elementary substances at one point of the sun's atmosphere, and their decomposition at another where the heat is more intense. It should be remembered in this connection that the meteorites have brought to us no new elements, and their evidence therefore, as far as it goes, points to the conclusion that the material of the sun would not differ essentially from that of the earth under the same conditions of temperature.

It thus appears that the dark and the bright lines are the same

phenomena seen under a different aspect, and the one as well as the other may be used to identify the different chemical elements. Hence, then, there must be both iron and sodium in the sun's atmosphere, and for the same reason we conclude that our luminary must contain hydrogen, calcium, magnesium, nickel, chromium, barium, copper, and zinc.

If next we turn the spectroscope on some of the brighter fixed stars, we see continuous spectra like the solar spectrum, of greater or less extent, and covered by dark lines. A careful comparison of these lines would seem to indicate that the stars differ very greatly from each other, although in general they are bodies similar to our sun; and if our theory is correct, we have been able to detect the presence of sodium, magnesium, hydrogen, calcium, iron, bismuth, tellurium, antimony, and mercury in Aldebaran, and other elements in other stars.

The most remarkable result of stellar chemistry remains yet to be noticed. On examining the nebulæ with the spectroscope, it has been found that, while some of them show a continuous spectrum, there are a number of these remarkable bodies which exhibit the phenomena of bright lines. This would lead us to the conclusion that the last are really, as the nebular theory assumes, masses of incandescent gas, while the first are not true nebulæ, but simply clusters of very distant stars. An examination of the comets has confirmed the previous conclusion that they also are mere masses of gas, but, singularly enough, the light from the coma of one of those bodies gave a continuous spectrum, due probably to reflected sunlight.

84. **Absorption Spectra.** — When a luminous flame is viewed with a spectroscope through solutions of various different substances, the otherwise continuous spectrum of the flame is seen to be interrupted by broad bands, which have a definite position, and are often a valuable means of recognizing the presence of such substances. This absorption spectrum, as it is called, is simply the reverse, the "negative," of the luminous spectrum of the same element.

For example, the salts of Didymium give a very characteristic and well-defined absorption spectrum, which is in fact

the only sure test we possess for this remarkable elementary substance; and as the bands may under some conditions be seen with reflected, as well as with transmitted light, we may apply the test even to opaque solids. Also, the same absorption bands are obtained either when the light is transmitted through a *liquid* solution, or through a *solid* crystal of *any* salt of the metal; and, moreover, the incandescent vapor of the metal shows bright bands corresponding to the dark bands in position. These facts would seem to show that the characteristic spectrum bands of an element may be, at least to some extent, independent both of the state of aggregation, and of the condition of combination of the elementary atoms.

Many substances besides the compounds of the element just noticed give characteristic absorption spectra, which have been found to be useful chemical tests, especially in the case of blood, and certain other bodies of organic origin. The most remarkable phenomena of this class are the absorption spectra which are seen when a luminous flame is viewed with a spectroscope through various colored vapors, such as those of nitric peroxide, bromine, and iodine. The dark bands are then very numerous, and in some cases may be resolved into well-defined lines. Indeed, the absorption bands are a class of phenomena closely allied to the Fraunhofer lines, many of which are known to result from the absorption by the earth's atmosphere of solar rays of certain degrees of refrangibility; and all these facts, with many others, prove that gases and vapors may exert their peculiar power of elective absorption at the ordinary temperature, as well as when incandescent. As a general rule, however, the absorption bands are not, like the bright lines of the metallic spectra or their representatives among the dark lines of the solar spectrum, definite images of the slit, but they are darker portions of the spectrum more or less regularly shaded, and correspond to the broad bands or luminous spaces in the spectra of the metallic vapors when not intensely heated. In each case the effect results from the blending of a greater or less number of images of the slit, differing in relative position and intensity.

85. **Theory of Exchanges.** — The facts of the last two sections

are all illustrations of a general principle already referred to in connection with the reversal of the sodium spectrum. This principle is known as the "Theory of Exchanges," and has been stated as follows: "The relation between the power of emission and power of absorption *for each kind of rays* (light or heat) is the same for all bodies at the same temperature. . . . . Let R denote the intensity of radiation of a particle for a given description of light at a given temperature, and let A denote the proportion of rays of this description incident on the particle which it absorbs; then $R \div A$ has the same value for all bodies at the same temperature, that is to say, this quotient is a function of the temperature only."

The law of exchanges finds its widest application in the phenomena of radiant heat, and so far as experiments have been made, it appears to be true in its greatest generality. In applying it to explain the reversal of the spectra of colored flames, we have only to deal with a single body in its relations to rays of different qualities. If the principle is true, the absorbing power of such a body at a given temperature must bear a fixed ratio to its power of emission for each kind of ray. If, for example, it has a great power of emitting certain rays of red light, it has a proportionally great power of absorbing the same rays. If, again, it has a feeble power of emitting violet rays of definite quality, its power of absorbing such rays is proportionally feeble, and bears the same ratio to the power of emission as before; and, lastly, it has no power of absorption over such rays as it does not itself emit. Moreover, it would follow that, although the relation of the absorbing to the radiating power might vary very greatly, so that, as the temperature falls, the last may become inconsiderable as compared with the first, or even vanish, no essential change in the character of the elective absorption would be thus induced. Hence, we should expect that bodies would absorb when cold rays of the same quality which they emit when hot, and also that opaque solids when heated would emit white light. We have seen that the general order of the phenomena is that which the law of exchanges would predict, and here, for the present, our knowledge stops. We have as yet

been able to form no satisfactory theory in regard to the relations of the molecular structure of bodies to the medium through which the waves of light or heat are transmitted. It is, however, worthy of notice that Euler, one of the earliest and ablest investigators of undulatory motion, predicted the discovery of the law of exchanges, in assuming, as a fundamental principle of the undulatory theory, that a body can only absorb oscillations isochronous with those of which it is itself susceptible.

86. **General Conclusions.** — The facts that have been stated in this chapter are sufficient to show that, although yet in its infancy, spectrum analysis promises to be one of the most powerful instruments of investigation ever applied in physical science. It seems to be the key which will in time open to our view the molecular structure of matter; and even now the results actually obtained suggest speculations of the most interesting character in regard to its ultimate constitution. The several monochromatic rays which the atoms of the elements emit must receive their peculiar character from some motion in the atoms themselves which is isochronous with the motion they impart. Is it not then in this motion that the *individuality* of the element resides, and may not all matter be alike in its ultimate essence? Such speculations, however wild, are not wholly unprofitable, if only they stimulate investigation, and thus lead to further discoveries.

87. **Index of Refraction, and Specific Refracting Power.** — The velocity of light, given in § 78 as 186,380 miles, or 299,940 kilometres per second, is the velocity *in vacuo*. The velocity as recently measured in air by Michelson is slightly less than this, — 299,864 kilometres per second, — and in general the velocity changes when the light passes from one medium into another, or from one portion to another of a medium which varies in density. When light passes from the air into a comparatively very dense medium, like water or glass, there is a great diminution of the velocity, and the ratio of the velocity in air, or more properly *in vacuo*, to the velocity in the medium is called the index of refraction of the medium. The index of refraction

for yellow light of a few well-known transparent media is as follows:—

Air,	1.0003	Fluor-Spar,	1.436	Sulphide of Carbon,	1.678
Water,	1.336	Olive Oil,	1.470	Ruby,	1.779
Alcohol,	1.372	Crown Glass,	1.534	Phosphorus,	2.224
Ether,	1.358	Flint Glass,	1.570	Diamond,	2.500

And the velocity of light in these media is easily found by dividing the velocity *in vacuo* given above by the index of refraction. When a ray of light passes from the air into a denser medium, like water or glass, which is bounded by a definite surface, it undergoes at this surface a sharp change of direction; and if, as usual, we call the angle made by the incident ray with a perpendicular or normal to the surface (at the point of contact) the angle of incidence, and the angle made by the refracted ray with the same normal (produced) the angle of refraction, we readily deduce another value for the index of refraction; and it is usually defined as the sine of the angle of incidence divided by the sine of the angle of refraction. Moreover, according to the well-known law of refraction, not only is this ratio constant for any incidence, but also the incident ray, the refracted ray, and the normal all lie in the same plane. We thus have

$$\mu = \frac{V}{V'} = \frac{\sin I}{\sin R},$$

an expression in which μ stands for the index of refraction, V and V' for the velocities of light in the two media, and I and R for the angles of incidence and refraction, as described above.

Furthermore, when a ray of light passes through a prism in a plane at right angles to the edge formed by the intersection of the refracting faces (the refracting edge of the prism, as it is called), and in such a direction that the angles made by the incident and emerging rays with the normals to the refracting faces are equal, then these rays subtend the smallest possible angle (for that prism), and this angle is called the angle of minimum deviation. If now we represent by A the angle between refracting faces (called the refracting angle of the prism),

by D the angle of minimum deviation, and by μ the index of refraction, as before, the following simple relation obtains between these quantities:—

$$\mu = \frac{\sin \frac{1}{2}(A + D)}{\sin \frac{1}{2} A}.$$

And since the refracting angle of the prism, as well as the angle of minimum deviation for any one of the rays of the spectrum, is easily measured, this formula gives us the means of determining the index of refraction of transparent substances. We either make a small prism of the material itself, or, if it is not a solid, we enclose the fluid in a prismatic cell of glass, the faces of which have been carefully ground and polished.

For the ether of space the value of the index of refraction is of course unity, and for any other medium the excess of the index over unity represents what we may call the refracting power of that medium. Now, since this refracting power increases directly with the density of the medium, independently of those specific characters which depend on its chemical composition, it is obvious that, if we divide the refracting power by the density (δ), we shall obtain a value from which the effect of density is as it were eliminated, and this quotient, $\frac{\mu - 1}{\delta}$, we call the specific refracting power of a substance; and if we multiply by the molecular weight of the substance, we have in $M\left(\frac{\mu - 1}{\delta}\right)$ the specific refracting power of the molecule, or, as it has been called, the refractive equivalent of the substance.

A comparison of the specific refracting powers of substances whose composition and molecular weights have been well determined shows that under similar circumstances a constant difference in the composition of the molecule corresponds to a constant difference in the specific refractive power. For example:—

Differing in Composition by C_1.

		$M\left(\frac{\mu-1}{\delta}\right)$	Diff.
Methyl Alcohol,	CH_4O	13.17	
Aldehyde,	C_2H_4O	18.58	5.41

Differing in Composition by H_2.

		$M\left(\frac{\mu-1}{\delta}\right)$	Diff.
Aldehyde,	C_2H_4O	18.58	
Ethyl Alcohol,	C_2H_6O	20.70	2.12

Differing in Composition by O_1.

Aldehyde,	$C_2H_4O_1$	18.58	
Acetic Acid,	$C_2H_4O_2$	21.11	2.53

The differences show the specific *refractive power* of one atom of carbon, one atom of oxygen, and two atoms of hydrogen; and the following values are, in each case, the mean of a very large number of comparisons similar to those just given.

	r_α	r_A
C,	5.0	4.86
H,	1.3	1.29
O,	3.0	2.90

Of course, these values are based on the determination of the index of refraction of each of the substances thus compared. The observations of density and of the index of refraction must be reduced to standard conditions, which may be arbitrarily selected, but in consequence of the very unequal and irregular dispersive power of the different substances, it is by no means a matter of indifference which of the lines of the spectrum is selected for the index of refraction. The correct way is to measure the index of refraction for at least four of the lines of the spectrum, which should be as widely distributed as possible, and the three hydrogen lines, together with the sodium line D, are well adapted to this purpose. Then, by a method devised by the French mathematician Cauchy, we can calculate the index of refraction corresponding to a wave of light of indefinite length, theoretically this is the value which ought to be used in calculations. The values in the column headed r_A above obtained in this way, but the results are nearly as satisfactory when deduced from indices observed with the red light of hydrogen spectrum.

A generalization of Landolt, which we have attempted to

explain in this section, may now be expressed in the following brief form: *The specific refractive power of a molecule is the sum of the refractive powers of its atoms.* The table given below shows how closely this generalization has been confirmed. The values of the molecular refractive power (R_a) calculated from the atomic composition by simply adding together the refractive powers of the several atoms (r_a) are here brought into comparison with the values deduced from direct observations of the densities and indices of refraction of the several compounds by means of the formula $M\left(\frac{\mu-1}{\delta}\right)$. We can give only a few of the very large number of results that have been collected.

		$M\left(\frac{\mu-1}{\delta}\right)$	R_a	Diff.
Propyl Alcohol,	C_3H_8O	28.6	28.4	+ 0.2
Propyl Aldehyde,	C_3H_6O	26.0	25.8	+ 0.2
Propyl-ethyl Ether,	$C_5H_{12}O$	43.8	43.6	+ 0.2
Propyl Acetate,	$C_5H_{10}O_2$	44.0	44.0	0.0
Propyl Chloride,	C_3H_7Cl	34.1	33.9	+ 0.2
Isobutyric Acid,	$C_4H_8O_2$	36.3	36.4	− 0.1
Hexan,	C_6H_{14}	48.6	48.2	+ 0.4
Triethylamine,	$C_6H_{15}N$	55.3	55.3	0.0

More recently it has been shown by Brühl that the atomic refractive power, although constant for all univalent atoms of the same kind, varies slightly for multivalent atoms, according to their relations to the molecular structure; but the student must refer to the original papers for a further discussion of the subject.

CHAPTER IV.

ELECTRICAL RELATIONS OF THE ATOMS.

88. **General Principles.**—If in a vessel of dilute sulphuric acid (one part of acid to twenty of water) we suspend a plate of zinc and a plate of platinum, opposite to each other, and not in contact, we find that no chemical action whatever takes place, provided the zinc and the acid are perfectly pure. As soon, however, as the two plates are united by a copper wire, as represented in Fig. 10, chemical action immediately ensues, and the following phenomena may be observed. First, bubbles of hydrogen gas are evolved from the surface of the platinum plate. Secondly, the zinc plate slowly dissolves, the zinc combining with the radical of the acid to form zincic sulphate, which is soluble in water. Lastly, a peculiar mode of atomic motion called electricity is transmitted through the copper wire, as may be made evident by appropriate means. If the connection between the plates is broken by dividing the conducting wire, the chemical action instantly stops, and the current of electricity ceases to flow; but as soon as the connection is renewed, these phenomena again appear.

Fig. 10.

Similar effects may be produced by other combinations than the one just mentioned, provided only certain conditions are realized. In the first place, the two plates must consist of materials which are unequally affected by the liquid contained in the vessel, or cell; and the greater the difference in this respect, within manageable limits, the better. In the second place, the materials, both of plates and connector, must be conductors of electricity; and, lastly, the liquid must contain some substance for one of whose radicals the material of one of the

plates has sufficient affinity to determine its decomposition under the conditions present. Such a combination is called a *Voltaic Cell.* The mode of action of this apparatus, which since its first discovery has been a subject of controversy, is very obscure, but the following theory gives an intelligible explanation of the general phenomena, and may serve a useful purpose until greater certainty can be attained.

89. **Polarity.**— The phenomena of magnetism have made us familiar with a condition of matter we call *polarity,* in which bodies manifest a mode of energy known as *polar force.* The characteristics of polar force are as follows:—

1. *The energy is chiefly concentrated at opposite points of the polarized body, called its poles.* 2. *The poles differ in kind in so far that, while unlike poles attract, like poles repel each other, and while unlike poles neutralize, like poles enhance each the other's effect.* 3. *With every pole is always associated its opposite, either on the same or a neighboring body, and in every polar system the sum* of the polar energies of one kind is exactly equal to that of those of the opposite kind.* 4. *A polarized body induces a similar state in all neighboring bodies susceptible of this condition, a pole of a given kind determining nearest to itself a pole of the opposite kind.* 5. *Induction is attended with no loss of energy in the inducing body, whose condition is frequently exalted by the reaction of the induced polarity.* 6. *Polarity appears of different kinds as well as in different degrees; the phenomena of magnetic, electrical, and chemical polarity, though similar in their general features, differing widely in their modes of manifestation.* 7. *Substances differ from each other, not only in their susceptibility to polarity of any given kind, but also in their power of retaining it.*†

The study of this class of phenomena has shown that the

* There may be several poles on the same mass of matter, and the polarity may be very irregularly distributed. Such is frequently the condition of the lodestone or of a steel bar irregularly magnetized.

† For example, the metals iron, nickel, and cobalt, with a few of their compounds, are the only substances susceptible of magnetic polarity to a high degree. Again, a hardened steel bar retains the polar condition more or less permanently, as in the common magnet, but soft iron loses its magnetic virtue the moment the inducing cause ceases to act.

energy manifested by polarized bodies is always the effect of an attraction or repulsion between poles, and that, whenever they appear to act on a neutral body, the last is always first polarized by induction. Thus the nails attracted by a magnet or the straws attracted by an electrified stick of sealing-wax are all in a polar condition. A horseshoe magnet, with its keeper attached, affords a familiar illustration of these principles, which will aid us in explaining the more obscure phenomena of the Voltaic cell. The horseshoe magnet was originally polarized by induction, and since it is made of hardened steel retains its magnetism. The soft-iron keeper while in contact with the magnet is as truly polarized as the steel. It has a north pole in contact with the south pole, and a south pole in contact with the north pole of the magnet. But the moment it is withdrawn, all its polarity disappears. Again, while the magnetic circuit, as we call it, is closed, the keeper, by reacting on the source of power, greatly enhances the energy of the magnet, which will lift a much greater weight suspended from the keeper than it can when the two poles act separately. Lastly, if we break a steel magnet, each of the parts will be found to be magnetized with poles relatively situated as is shown in Fig. 11; and since this relation of parts is preserved, however far we may carry the subdivision, we are led to the conclusion that the polarity is a quality inherent, not in the bar as a whole, but in the molecules of which it consists, and picture to ourselves as the condition of a magnetized bar that which is rudely represented in Fig. 12.

Fig. 11.

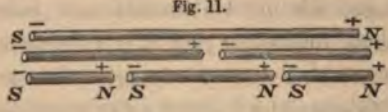


Fig. 12.

90. **Theory of Chemical Polarity.** — As the molecules of iron may be magnetically polarized, we infer that the molecules of all substances are susceptible of different polar states, and we conceive that chemism* is a manifestation of a molecular condition

* term is synonymous with the old term *chemical affinity*, to which it is accounts to be preferred.

which we may distinguish as chemical polarity. It must be remembered, however, that we do not understand the cause of the differences in the various modes of polar energy; and in saying that the molecules of matter may be chemically polarized, we mean merely that they are susceptible of a condition whose general features have been indicated above. Our theory further assumes that, while with some molecules the polarity is inherent, and therefore permanent, with others it can only be induced by extraneous causes. Molecules not normally polarized may, however, become polarized by induction to as high a degree as those in which polarity is inherent, or even a higher one, but their polarity, like that of an electromagnet, is transient, varying with the inducing cause. Again, as every analogy would lead us to believe, our theory further assumes that different substances are susceptible of chemical polarity (whether it be inherent or induced) to very different degrees, and that the susceptibility varies under different conditions. Lastly, our theory supposes that the chemical activity of a substance depends on the degree of polarity inherent in its molecules; and it refers the well-known active qualities of acids and alkalies to the fact that their peculiar constitution renders their molecules strongly polarized, while the inert character of most of the elementary substances is explained by the neutral condition which their homogeneous structures would naturally produce in their molecules. Thus, for example, we suppose that every molecule of sulphuric acid, $H_2{}^{=}SO_4$, or of hydrochloric acid, *H-Cl*, or of sodic hydrate, *H-NaO*, is naturally polarized, while, on the other hand, the molecules of zinc, *Zn*, of magnesium, *Mg*, of hydrogen, *H-H*, and of oxygen, $O^{=}O$, are all normally neutral. As soon, however, as we place zinc in contact with dilute sulphuric acid, the metallic molecules become polarized by induction to the degree of which they are susceptible under the influence of this acid. A powerful attraction is thus developed, of which the familiar chemical reaction is the result. If magnesium is treated in a similar way, the action is more energetic, because, as we suppose, the molecules of this metal are susceptible of a higher degree of polarity, and the force developed is therefore proportionally stronger. On the other

hand, with metallic copper there is no action under the same conditions, because the molecules of the metal do not acquire a sufficient degree of polarity to determine chemical change.

While, however, the molecular structure appears to be the most important, it is evidently by no means the only cause which determines chemical polarity. The highly active qualities of the alkaline metals and of the chlorine group of elementary substances indicate that their molecules, although apparently homogeneous in structure, must be permanently polarized. Moreover, the fact that a high degree of energy is developed in many of the elementary substances, as in oxygen gas, by a simple elevation of temperature, and the general principle that heat hastens chemical changes, seem to indicate that the polar condition may be frequently produced by this agent alone. So also the process of photography is most simply explained by the theory that the sun's rays excite a similar condition in the silver compounds on the surface of the sensitive plate; and the effect of continuous electrical discharges in converting oxygen gas into that peculiar active modification of this substance called ozone may be regarded as a direct result of their polarizing power.

91. **Theory of Electricity.**—The study of the phenomena of optics has led physicists to the conclusion that there exists throughout space, filling not only the interplanetary but also the intermolecular spaces, a highly attenuated but at the same time wonderfully elastic medium, which is called the ether (§ 78). Again, the phenomena of heat indicate that the molecular forces have an energy which is adequate to cope with this very great elasticity; and we can conceive that they condense around these molecules greater or less quantities of this ether, thus giving to each a distinct atmosphere, but one which merges into that universally diffused medium in which molecule and planet alike float. Now our theory supposes that electrical phenomena are caused by disturbances in the composition of these ethereal atmospheres. The electrical ether,* as we assume, consists of two separable

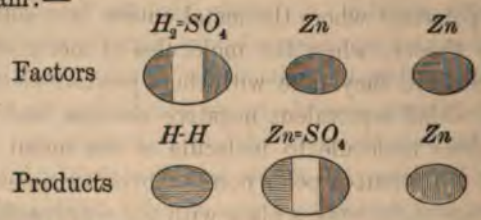
* As it is not important for our present purpose to inquire whether the electrical ether is identical or only is mingled with the luminiferous ether, this question is here left in abeyance.

materials, which, adopting names long used in science, we will call positive and negative, or vitreous and resinous electricities. In all the terrestrial region of the solar system, at least, these electricities are blended in certain definite proportions, like the constituents of the earth's atmosphere, but by various causes they may become separated and more or less isolated, either on the same or on different molecules. Whenever this takes place, the two electricities tend to flow together until the normal condition is restored, in accordance with the law of diffusion; but the force of diffusion in these molecular atmospheres is vastly greater, and the process vastly more rapid, than it is in the terrestrial atmosphere, because the elasticity of the ether so greatly exceeds that of the air. This being granted, our theory further supposes that every process of electrical excitement causes a separation of the constituents of the ether, and that an electrified body is one on whose molecules one or the other of the two electricities is to a greater or less degree isolated; and again, that the familiar phenomena of attraction and repulsion between electrified bodies are the effects of pressure caused by the diffusive force; and lastly, that an electrical current consists in an actual transfer of the ethereal material between the molecules of the conductor. We have not space, however, to follow out the theory into its mechanical details, and we must content ourselves with applying it to the explanation of the phenomena of the Voltaic cell.

92. **Theory of the Voltaic Cell.**— In studying chemical reactions we have thus far overlooked the molecular atmospheres; but it is evident that, if the above theory is correct, they must enter as important factors into every chemical change. This theory assumes that the condition of the atmosphere is intimately connected with that of the molecule, although in what way it does not attempt to explain. When the molecule is polarized, the two electricities are more or less fully separated and isolated around the molecular poles; and if the polarity is inherent, this condition is permanent. If, however, the polar state is induced, the neutral condition is restored as soon as the inducing force ceases to act. Let us study now from this new point of view the familiar reaction of sulphuric acid on zinc referred to above.

$$Zn + (H_2SO_4 + Aq) = (ZnSO_4 + Aq) + H\text{-}H.$$

The molecule H_2SO_4 is inherently polarized, and induces at once a similar condition in the normally neutral molecule Zn. At the poles of each of these molecules we have therefore free electricity. When now Zn replaces H_2 in H_2SO_4 it takes with it into its new combination only free positive electricity, leaving behind the corresponding negative electricity on the adjacent molecule of zinc. Meanwhile the hydrogen atoms thus liberated bring with them to form the molecule H-H only positive electricity. We have thus set free on opposite molecules at the same time equivalent quantities of the two electricities, and, the equilibrium being thus disturbed, an interchange at once takes place between them, by which the normal condition of their atmospheres is restored. In order to make this point clearer, we have endeavored to illustrate the reaction in the following diagram:—



This diagram, however, indicates very imperfectly the conception we have formed of the process, and there are certain quantitative relations between the parts which must not be overlooked, although they can be as yet but very imperfectly understood. We should naturally infer that the quantity of ethereal atmosphere would be determined in every case by the mass of the molecule, but the quantities of free electricities separated from this atmosphere under different conditions seem to depend on the atomicities of the radicals of which the molecule consists. At least, the facts indicate that the amount of free electricity which any group of atoms takes out of the molecule from which it is parted is exactly measured by the number of atomic bonds thus broken. Hence in our diagram the amount of positive electricity which H_2 takes from H_2SO_4 is a definite quantity, and

exactly equal to that which Zn carries in to take its place. Moreover, this last quantity came originally, not from one, but from two zinc molecules, and the chemical metathesis between H_2 and Zn was accompanied by an interchange of electricities between the zinc molecules, by which all the free positive electricity passed to the one which entered into combination, and all the free negative electricity to the one left behind; and further, as already stated, this free negative electricity is equivalent to the free positive electricity on the hydrogen molecule formed at the same time.

If, as in the usual form of the reaction we have been studying, the acid sufficiently diluted is poured upon clippings of sheet zinc, it is found that, although the mass of the metal is polarized throughout, the polarity is very irregularly distributed. A multitude of negative polar points are formed upon the surface, from which bubbles of hydrogen gas are evolved, and around these are spaces positively polarized where the metal enters into solution. According to our theory, when the molecules of metal replace the atoms of hydrogen, they take with them positive electrical charges, leaving behind equivalent negative charges, and these are transmitted from molecule to molecule of the metal, until they reach one of the negative polar points above mentioned. It is there that the interchange takes place with the positive charges on the molecules of hydrogen gas as rapidly as these are formed. The polar points just referred to appear to be determined by variations of texture or bits of impurity in the metal, and this is the reason that the general polarity of the mass is so irregularly distributed. If the metal is absolutely pure and uniform in texture, or if the surface of the common sheet zinc is previously amalgamated, there is no local action, and the zinc will not dissolve unless we fasten to the metal a piece of some material less readily acted on by the acid, which must be also a conductor of electricity. But when this is done, the whole mass becomes polarized uniformly throughout, after the pattern represented in Fig. 12. Of this system the surface of the zinc forms the positive pole, and the surface of the second material the negative pole. Chemical action ensues as before, and while zinc dissolves

at the positive pole, hydrogen gas is evolved from the negative pole.

We are now prepared to understand the conditions in the Voltaic cell represented in Fig. 10. Here we have a plate of zinc and a plate of platinum, united by a metallic wire and dipping together into the acid liquid, with their surfaces opposed to each other and not touching. Here, also, the two plates with the conductor form one uniformly polarized system, of which the surface of the zinc is the positive, and the surface of the platinum the negative pole. The polarity of this arrangement is induced by the action of the acid, whose molecules are inherently polarized. Moreover, under these conditions the mass of acid between the plates forms also a uniformly polarized system, the molecules arranging themselves in polar lines, as represented in Fig. 13. We may compare the combination thus formed to a magnetic circuit, consisting of a horseshoe magnet and its armature, or rather of a bar magnet with a horseshoe armature. The inherently polarized liquid corresponds to the permanent magnet, the system of metallic plates to the armature with its induced polarity. Now just as in the magnetic circuit we have a strong attractive force at the surfaces where the armature touches the magnet, so in the Voltaic circuit we have a powerful force exerted at each of the corresponding surfaces. A mutual attraction is exerted between the hydrogen end of the acid molecules and the platinum surface on one side, and the sulphion end * of the same molecules and the zinc surface on the other side. These forces are adequate to decompose the acid. The sulphion atoms enter into union with the zinc to form zinc sulphate, which dissolves in the acid liquid, while the hydrogen atoms combine with each other to form molecules of hydrogen gas, which collects in bubbles that rise along the surface of the platinum plate. Meanwhile, every molecule of zinc which enters into solution leaves behind a charge of negative electricity, and every molecule of hydrogen gas carries to the surface of the

Fig. 13.

* For the sake of simplicity we have represented in the figures molecules of *H-Cl* instead of $H_2{}^{\cdot}SO_4$, but the theory applies equally to both.

platinum plate a charge of positive electricity, and these opposite charges flow together through the conductor, forming what we call an electrical current, which tends to restore the electrical equilibrium that the chemical action destroys.

93. **Electrical Current.** — According to our theory an electrical current consists, in the last analysis, in the transfer of the ethereal medium between neighboring molecules, the one giving up a quantity of positive electricity and receiving an equivalent portion of negative electricity in its stead. This transfer is supposed to take place at the surface of contact between the molecular atmospheres by a process similar to diffusion (§ 63), and implies an oscillation of the molecules by which each is brought alternately in near proximity to its neighbors on either side. The oscillatory motion is maintained by the alternate attractions and repulsions, which the varying phases of the molecules necessarily determine, and is a most important element of the electrical current. It can easily be imitated by suspending with silk threads small metallic balls between two brass knobs connected with the conductors of an electrical machine, so that they hang near, and at equal distances from each other, on the same line. The continuous oscillation of these balls, while the machine is in action, illustrates what we conceive to be the mode of motion in the molecules of a conductor.

If the above explanation is correct, it is obvious that an electrical current in a solid conductor has two distinct elements: first, an oscillatory motion of the molecules; secondly, a mutual transfer of the two modifications of the electrical ether from molecule to molecule, along the lines uniting the opposite poles of the polar system, which every current implies. But in the acid liquid, which not only originates the current but also forms a part of the circuit, the relations are somewhat different. There the transfer of the two electricities is attended with a decomposition of the acid molecules, and the opposed atoms, each bearing its charge of electricity, actually travel from one plate to the other. Thus we have the singular phenomenon produced of two coexisting atomic currents throughout the mass of the liquid, a stream of sulphion atoms constantly setting towards the zinc

plate, and a stream of hydrogen atoms flowing in the opposite direction, in parallel lines, towards the platinum plate. The result is produced by a constant metathesis along the whole line of molecules between the two plates, so that for every atom of sulphion which enters into union with the zinc a double atom or molecule of hydrogen is set free at the face of the platinum plate.

As our theory shows, the opposite currents of atoms in the liquid and the opposite currents of electricity in the solid conductor are mutually dependent. Hence, if the connection is broken, so that the motion can no longer be transmitted through the conductor, the motion in the liquid itself ceases; and if by any means the motion through the conductor is checked, the motion of the atoms in the liquid is reduced to the same extent. The two currents, which, as we have seen, are continuous throughout the whole circuit, take the names of the two kinds of electricity which they respectively carry; that flowing into the conducting wire from the platinum, or inactive plate, being called the positive current, and that from the zinc, or active plate, the negative current. Reasoning from certain mechanical phenomena, the physicists originally concluded that the electrical current flowed in but one direction, that is, through the conducting wire from the platinum plate to the zinc, and from the zinc plate through the liquid back again to the platinum; and now, when the direction of the current is spoken of, it is this direction, that of the positive current, which is always meant.

94. **Electrical Conducting Power, or Resistance.** — Different materials transmit the electric current with very different degrees of facility; for while in some this peculiar form of molecular motion is easily maintained, in others the molecules yield to it only with difficulty, and many substances seem not to be susceptible of it. The conducting powers of different metallic wires have been very carefully studied, and some of the most trustworthy results are collected in the following table. Silver is the best conductor known, and, assuming that a silver wire of definite size and 100 centimetres long is taken as the standard, the number opposite the name of each metal is the length in centimetres of a wire made of this metal, and of the same size

as the first, which will oppose the same resistance to the transmission of the current. The second column gives the relative resistances of wires of the same materials when of equal size and of equal length. The relative or *specific resistances* of two such wires must evidently be inversely proportional to their conducting powers, and thus the numbers of the second column are easily calculated from those of the first. For the results collated in this table we are indebted to the careful investigations of Professor Matthiessen.

Pure Metals.	Conducting Power.		Specific Resistance.	
	At 0°.	At 100°.	At 0°.	At 100°.
Silver (*hard drawn*)	100.00	71.56	1.000	1.397
Copper (*hard drawn*)	99.95	70.27	1.0005	1.423
Gold (*hard drawn*)	77.96	55.90	1.283	1.788
Zinc	29.02	20.67	3.445	4.838
Cadmium	23.72	16.77	4.216	5.964
Cobalt	17.22		5.808	
Iron (*hard drawn*)	16.81		5.948	
Nickel	13.11		7.628	
Tin	12.36	8.67	8.091	11.53
Thallium	9.16		10.92	
Lead	8.32	5.86	12.02	17.06
Arsenic	4.76	3.33	21.01	30.03
Antimony	4.62	3.26	21.65	30.68
Bismuth	1.245	0.878	80.34	113.9

Commercial Metals.	C. P.	Sp. R.	C°.	Commercial Metals.	C. P.	Sp. R.	C°.
Copper	77.43	1.291	18.8	Iron	14.44	6.924	20.4
Sodium	37.43	2.672	21.7	Palladium	12.64	7.911	17.2
Aluminum	33.76	2.962	19.5	Platinum	10.53	9.497	20.7
Magnesium	25.47	3.926	17.0	Strontium	6.71	14.90	20.5
Calcium	22.14	4.516	16.8	Mercury	1.63	61.35	22.8
Potassium	20.85	4.795	20.4	Tellurium	0.00077	129,800	19.6
Lithium	19.00	5.262	20.0	Red Phosphorus	0.00000123	81,300,000	24.0

If, next, we compare wires of the same material, but of different sizes, we find that the resistance increases as the length, and diminishes as the area of the section. Moreover, if we adopt some absolute standard of resistance, like that selected by the English physicists, we can easily express the resistance of any given conductor in terms of this unit. It must be remembered, however, in making such comparisons, that the resistance varies with the temperature, and also that the conducting power

of the same metal is materially influenced both by its physical condition and by the presence of impurities.

95. **Ohm's Law.** — The first effect of the chemical forces in the cell of an electrical combination is to marshal the dissimilar atoms of the active liquid between the plates into lines, which at once begin to move in parallel columns, but in opposite directions (Fig. 13). Moreover, each one of these lines of *moving* atoms is continued by a corresponding line of *oscillating* atoms in the conducting wire, and thus is formed a continuous circuit returning upon itself. The union of all the *lines of force* in the two opposite coexisting streams constitutes in any case the electrical current, and the different parts of this continuous chain are so related that *the total amount of motion is always the same at every point on the circuit*, and *no more lines of moving atoms form in the liquid between the plates than can be continued through the oscillating atoms of the solid conductors.*

If we adopt this theory, it is obvious that the strength of any electrical current must depend, first, on the number of continuous lines of force, and, secondly, on the strength of the polarity transmitted through each of these channels. Of these two elements, the first is determined solely by the total resistance which the various parts of the circuit oppose to the electrical motion, and the greater this resistance the less will be the number of the lines of force. The second element is determined by the value of the resultants of all the polar forces acting in any combination, which draw the dissimilar atoms towards the opposite plates, — a value which depends solely on *the chemical relations of the materials of the plates to that of the active liquid*, and is what is called the *electromotive force* of the combination, a quantity we will represent by E.

It appears, then, from the above analysis, that an electrical current is a continuous chain, which is sustained in a regulated and equable motion in all its parts by the chemical activity in the cell, and that the strength of this current at any point of the chain must be directly proportional to the electromotive force, and inversely proportional to the sum of the resistances throughout the circuit. If, then, we represent the resistance in the con-

ducting wire by r, the resistance of the liquid between the plates of the cell by R,* and also the strength of the current by C, we shall have, in every case,

$$C = \frac{E}{R + r}. \qquad [58]$$

The quantities C, R, r, and E may all be accurately measured, and stand in each case for a certain number of arbitrary units, whose relations will hereafter be stated.

96. **Electromotive Force and Strength of Current.** — It would seem at first sight as if the strength of an electric current might be increased by simply enlarging the size of the plates in the combination employed, and obviously the number of *possible* lines of moving atoms which could be marshalled in the liquid between the plates would thus be increased; but, as has been stated, the parts of the circuit are so intimately connected that no greater number of lines of atoms can form between the plates than can be continued through the whole circuit, and practically there may be formed between the smallest plates a vastly greater number of atomic lines than can be continued through any conductor, however good its quality or however ample its size. Hence it is that by increasing the size of the plates we multiply the lines of force only in so far as we thereby lessen the resistance in the liquid part of the circuit. We thus simply lessen the value of R in Ohm's formula [58]; but if this value is already small as compared with r, that is, if the resistance in the cell is small compared with that in the conductor, no material gain in the power of the current, or in the value of C, will result. On the other hand, if the exterior resistance, r, is small, or nearly nothing, as when the plates are connected by a thick

* The resistance of any circuit may be conveniently divided into two parts, first, the resistance of the conducting wire, and, secondly, the resistance of the liquid portion of the circuit between the two plates of the cell. The resistance of the solid conductor may be readily estimated on the principles stated in the last section, and the resistance of the liquid may be measured in a similar way. The last depends, — 1. On the conducting power of the liquid; 2. On the length of the liquid circuit, which is determined by the distance apart of the plates; 3. On the area of the section of the liquid conductor, which is determined by the size of the plates; and, 4. On the temperature.

metallic conductor, then the value of C will increase in very nearly the same proportion as the size of the plates is enlarged, and the value of R, in consequence, diminished. Under these conditions, the number of lines of moving atoms is greatly multiplied, and we obtain a current of very great volume, but only flowing with the limited force which the single cell is capable of maintaining. Such a current has but little power of overcoming obstacles; and if we attempt to condense it by using a smaller conductor, we reduce, as has been said, the chemical action which keeps the whole in motion, and thus lessen the volume of the flow. This is generally expressed by saying that the current has large *quantity*, but small *intensity*, or (more properly) small *electromotive power*.

It must now be obvious from the theory, that we cannot increase effectively the intensity of a current (its power of overcoming obstacles) without in some way increasing the chemical activity, or, in other words, the electromotive force of the combination employed, and Ohm's formula leads to the same result. If the value of r in our formula is very large as compared with R, we cannot increase it still further without lessening the total value, C, unless at the same time we increase the value of E. Now, this electromotive force may be, to a certain extent, increased by using a more active combination; but the limit in this direction is soon reached, and the construction of the cell which has been found practically to be the most efficient will be described below.

We can, however, increase the effective electromotive force to almost any extent by using a number of cells, and coupling them together in the manner represented by Fig. 14, the platinum plate of the first cell being united by a large metallic connector to the zinc plate of the second, and so on through the line, until finally the external conductor establishes a connection between the platinum plate of the last cell and the zinc plate of the first. Such a combination as this is called a Galvanic or Voltaic * battery, and the current which flows through such a

* From the names of Galvani and Volta, two Italian physicists, who first investigated this class of phenomena.

combination has a vastly greater power of overcoming resistance than that of any single cell, however large.

The increased effect obtained with such a combination will be easily understood when it is remembered that each of the innumerable closed chains of moving molecules now extends through the whole combination, and that all its parts move in the same close mutual dependence as before. But whereas with a single cell the motion throughout any single chain of molecules is sustained by the chemical energy at only one point, it is here reinforced at several points; and the polar energy at any point of the circuit is the effect of the induction of the acid molecules between each pair of plates concurring with that produced by the similar molecules between every other pair. The electromotive power is then increased in proportion to the number of cells; and the effect on the current would be increased in the same proportion, were it not for the fact that the current must keep in motion a greater mass of liquid, and hence the resistance is increased at the same time. The value of this resistance, however, is easily estimated, since it is directly proportional to the distance through which the current has to flow in the liquid; and hence, if the liquid is the same in all the cells, and the plates are at the same distance apart in each, the liquid resistance will be n times as great in a combination of n cells as it is in one. Moreover, since the effective electromotive force is n times as great also, while the external resistance remains unchanged, the strength of the current from such a combination will still be expressed by formula [58], slightly modified:—

Fig. 14.

$$C = \frac{nE}{nR + r}. \qquad [59]$$

This formula shows at once that, when the exterior resistance is very small, or nothing, very little or no gain will result from increasing the number of cells, for the ratio of nE to nR is the same as that of E to R; and under such conditions, in order to increase the strength of the current we must increase the sur-

face of the plates. If, on the contrary, the exterior resistance is very large, the formula shows that great gain will result from increasing the number of the cells, and that little or no advantage will accrue from enlarging the surface of the plates. Moreover, the formula enables us in any case to determine what proportion the number of cells should bear to the size of the plates in order to obtain the full effect of any battery in doing a given work; and in the numerous applications of electricity in the arts we find abundant illustrations of the principles it involves. The methods used in finding the values of the quantities represented in the formula lie beyond the scope of this work, and for such information the student is referred to works on Physics.

97. **Construction of Cells.** — It is found practically that the simple combination of plates and acid first described must be slightly modified in order to obtain the best results.

In the first place, both the zinc and sulphuric acid of commerce contain impurities, which give rise to what is called local action, and cause the zinc to dissolve in the acid when the battery is not in action. Fortunately, however, it has been found that such local action can be wholly prevented by carefully amalgamating the surface of the zinc and filtering the acidulated water. The mercury on the surface of the zinc plates acts as a solvent, and gives a certain freedom of motion to the particles of the metal. These, by the action of the polar forces, are brought to the surface of the plate, while the impurities are forced back towards the interior, so that the plate constantly exposes a surface of pure zinc to the action of the acid. By filtering we remove the particles of plumbic sulphate which remain floating in the sulphuric acid for a long time after it has been diluted with water, and which, when deposited on the surface of the zinc, become points of local action, even when the plates have been carefully amalgamated.

In the second place, the continued action of the simple combination first described develops conditions which soon greatly impair, and at last wholly destroy, its efficiency. The hydrogen gas which by the action of the current is evolved at the platinum

plate adheres strongly to its surface, and with its powerful affinities draws back the lines of atoms moving towards the zinc plate, and thus diminishes the effective electromotive force. Moreover, after the battery has been working for some time, the water becomes charged with zinc sulphate; and then the zinc, following the course of the hydrogen, is also deposited on the surface of the platinum, which after a while becomes, to all intents and purposes, a second zinc plate, and then, of course, the electric current ceases.

Both of these difficulties, however, have also been surmounted by the very simple arrangement made by Mr. Grove, of London. The Grove cell (Fig. 15) consists of a circular plate of zinc well amalgamated on its surface, and immersed in a glass jar containing dilute sulphuric acid. Within this zinc cylinder is placed a cylindrical vessel of much smaller diameter, made of porous earthenware, and filled with the strongest nitric acid, and in this hangs the plate of platinum (Fig. 16). The walls of the

Fig. 15.

Fig. 16.

porous cell allow both the hydrogen and the zinc atoms to pass freely on their way to the platinum plate; but the moment they reach the nitric acid they are at once oxidized, and thus the surface of the platinum is kept clean, and the cell in condition to exert its maximum electromotive power. In this combination we may substitute for the plate of platinum a plate of dense coke, such as forms in the interior of gas retorts, which is

very much cheaper, and enables us to construct large cells at a moderate cost. The use of gas coke was first suggested by Professor Bunsen of Heidelberg, and the cell so constructed generally bears his name. The Bunsen cell, such as is represented in Fig. 17, is exceedingly well adapted for use in the laboratory. These cells are usually made of nearly a uniform size, the zinc

Fig. 17.

cylinders being about 8 c. m. in diameter by 22 c. m. high, and they are frequently referred to as a rough standard of electrical power. They may be united so as to produce effects either of intensity or of quantity. The intensity effects are obtained in the manner already described (see Fig. 14); and the quantity effects are obtained with equal readiness, since, by attaching the zinc of several cells to the same metallic conductor, and the corresponding coke plates to a similar conductor, we have the equivalent of one cell with large plates. Many other forms of battery, differing in more or less important details from those here described, and adapted to special applications of electricity, are used in the arts, and are fully described in the larger works on Physics.

98. **Electrolysis.** — As our theory indicates, the electrical current has the remarkable power of imparting to the unlike atoms of almost all compound bodies motion in opposite directions, like that in the battery cell itself, and this, too, at whatever point in the circuit they may be introduced. The Galvanic battery thus becomes a most potent agent in producing chemical decompositions, and it is in consequence of this fact that the

theory of the instrument fills such an important place in the philosophy of chemistry.

If we break the metallic conductor at any point of a closed circuit, the two ends, which in chemical experiments we usually arm with platinum plates,* are called poles. The end connected with the platinum or coke plate, from which the positive current is assumed to flow, is called the *positive pole*, and the end connected with the zinc plate, from which the negative current flows, is called the *negative pole*. Let us assume that Fig. 18 represents the two platinum poles dipping in a solution of hydrochloric acid in water, which thus becomes a part of the circuit. The moment the circuit is thus closed, the *H* and *Cl* atoms begin to travel in opposite directions, just as in the battery cell below. The hydrogen atoms move *with the positive current* towards the negative pole, and hydrogen gas is disengaged from the surface of the negative plate, while the chlorine atoms move *with the negative current* towards the positive pole, and chlorine gas is evolved from the surface of the positive plate. Moreover, it will be noticed that each kind of atoms moves in the same direction on the closed circuit, that is, follows the course of the same current, both in the battery cell below and in the decomposing cell above; and wherever we break the circuit, and at as many places as we may break it, the same phenomena may be produced, provided only that our battery has sufficient power to overcome the resistance thus introduced.

Fig. 18.

If next we dip the poles in water, the atoms of the water will be set moving, as shown in Fig. 19; hydrogen gas escaping as before from the negative pole, and oxygen gas from the positive. We find, however, that pure water opposes a very great resistance to the motion of the current; and unless the current has great intensity, the effects obtained are inconsiderable. But if we mix with the water a little sulphuric acid, the decomposition

* We use platinum plates because this metal does not readily enter into combination with the ordinary chemical agents.

at once becomes very rapid; but then it is the atoms of the sulphuric acid, and not those of the water, which are set in motion. The molecule H_2SO_4 divides into H_2 and SO_4; the hydrogen atoms moving in the usual direction, and the atoms of SO_4 in the opposite direction. As soon, however, as the last are set free at the positive pole, they come in contact with water, which they immediately decompose,

Fig. 19.

$$2\,H_2O + 2\,SO_4 = 2\,H_2SO_4 + O{=}O,$$

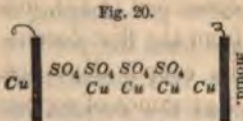
and the oxygen gas thus generated escapes from the surface of the platinum plate. Thus the result is the same as if water were directly decomposed, but the actual process is quite different.

So also in many other cases of electrolysis, — as these decompositions by the electrical current are called, — the process is complicated by the action of the water, which is the usual medium employed in the experiments. Thus, if we interpose between the poles a solution of common salt, $NaCl$, the chlorine atoms move towards the positive pole, and chlorine gas is there evolved, as in the first example. The sodium atoms move also, but in the opposite direction. As soon, however, as they are set free at the negative pole, they decompose the water present; hydrogen gas is formed, which escapes in bubbles from the platinum plate, while sodic hydrate (caustic soda) remains in solution,

$$2\,H_2O + 2\,Na = 2\,H{,}Na{-}O + H{-}H.$$

We add but one other example, which illustrates a very important application of these principles in the arts. We assume, in Fig. 20, that the positive pole is armed with a plate of copper, and that to the negative pole has been fastened a mould of some medallion we wish to copy, the surface of which, at least, is a good conductor. We assume, further, that both copper plate and mould are suspended in a solution of sulphate of copper, $Cu{=}SO_4$. In this case the atoms of the compound are set in motion as before. Those of copper accumulate on the

Fig. 20.



surface of the mould; and at last the coating will attain such thickness that it can be removed, furnishing an exact copy of the original medallion. Meanwhile the atoms of SO_4 have found at the positive pole a mass of copper, with whose atoms they have combined; and thus fresh sulphate of copper has been formed, and the solution replenished. The process has in effect consisted in a transfer of metal from the copper plate to the medallion; and, by using appropriate solvents, silver and gold can be transferred and deposited in the same way.

In all these processes of electrolysis one remarkable fact has been observed, which has a very important bearing on the theory of the battery. If in any given circuit we introduce a number of decomposing cells containing acidulated water, we find that in a given time exactly the same amount of gas is evolved in each; thus proving, what we have thus far assumed, that the moving power is absolutely the same at all points on the circuit. Moreover, the amount of gas which is evolved from such a decomposing cell in the unit of time is an accurate measure of the strength of the current actually flowing in any circuit, and this mode of measuring the quantity of an electrical current is constantly used.

We should infer from the facts already stated, and the principle has been confirmed by the most careful experiments, that the chemical changes which may take place at different points of the same closed circuit are always the exact equivalents of each other. If, for example, we have a series of Grove cells, arranged as in Fig. 14, and interpose in the external circuit two decomposing cells, as in Figs. 19 and 20, we shall find (provided there is no local action) that the weight of zinc dissolved in each of the five Grove cells is the exact *chemical equivalent* (§ 27), not only of the weight of hydrogen gas evolved from the first decomposing cell, but also of the weight of metallic copper deposited on the mould in the second. For every 63.4 grammes of copper deposited, 2 grammes of hydrogen are evolved, and 65.2 grammes of zinc are dissolved in *each* cell of the battery. If there is also local action in the cells, the chemical change thus induced is added to the normal effect of the battery current.

This important principle (discovered by Faraday) is in entire harmony with the theory of electricity developed in this chapter. In the single Voltaic cell (Fig. 10) there is but one source of free electricity, which all flows through the same conductor. In a Voltaic battery (Fig. 14) there are as many sources of free electricity as there are separate cells; but only the free electricity received on the end plates flows through the longer conductor,* for that received on the intermediate plates becomes neutralized in the shorter conductors * uniting the cells. In either case, if a liquid forms a part of the principal conductor, as in Fig. 18, then the molecules of the liquid decomposed by the current become an additional source of electricity, and the currents flowing from the two ends of the battery are neutralized by the charges of electricity which the atoms liberated from the electrolyte † bring with them to either electrode.† Thus, in Fig. 18, the positive electricity flowing from the inactive plate of the battery is neutralized by the negative electricity which the chlorine atoms yield, and the negative electricity from the active plate of the battery by the positive electricity which the hydrogen atoms yield. Now since, according to our theory, the strength of a current is necessarily the same at all points of a continuous circuit, however extended, and since the amount of electricity set free in the decomposing cell, as in the battery cells, must be proportional to the number of atomic bonds broken (§ 88), it is evident that it would require, for example, twice as many hydrogen as copper atoms, liberated on the face of an electrode in a given time, to supply the same current, and this is equivalent to the principle stated above.

The examples which have been given are sufficient to illustrate the remarkable power which the electric current possesses of setting in motion the atoms of compound bodies. Innumerable experiments have shown that, in reference to their relations to the current, the atoms, both simple and compound, may be

* It will be noticed that each of the five conductors in Fig. 14 sustains the same relations to the battery as a whole.

† The liquid submitted to electrolysis is frequently called an *electrolyte*, and the inactive poles dipping into the liquid are also called *electrodes*.

divided into two great classes: first, those which travel on the line of the circuit in the direction of the positive current, and follow in the lead of the hydrogen atoms; and, secondly, those which follow the lead of the chlorine atoms, and move in the opposite direction with the negative current. The first class of atoms, or radicals, we call *positive;* and the second class, *negative.*

The opposition in qualities of the chemical atoms, which the study of these electrical phenomena has revealed, is, in many cases at least, relative, and not absolute. For while there are some atoms which always manifest the same character, there are others which appear in some associations positive and in other associations negative. To such an extent is this true, that the electrical relations of the atoms are best shown by grouping the elements in series, which may be so arranged that each member of the series shall be electro-positive when in combination with those elements which follow it, and electro-negative when combined with those which precede it.

ELECTRICAL MEASUREMENTS.

99. **Fundamental Laws.** — The following formulæ express the most important properties of electrical currents: —

$$(1.)\quad C = F\frac{K^2}{Lm} \qquad (2.)\quad C = \frac{E}{R} \qquad (3.)\quad Q = Ct$$

$$(4.)\quad W = C^2Rt \qquad (5.)\quad W = QE$$

The first defines strength of current as a magnitude proportional to the force which it exerts on a magnetic pole under constant conditions. These conditions are the strength of pole, m, the length of the conductor, L, — assumed, as in the common form of galvanometer, to be bent in a circle around the pole, — and the radius of this circle, K. The unit of force is that force which imparts to one gramme of matter the velocity of one metre in one second, and the unit pole that pole which at a distance of one metre repels a similar and equal pole with the unit force.

The second is Ohm's formula (§ 95), and expresses the principle, which can be readily demonstrated experimentally, that the strength of current, as defined by (1), is directly proportional to the electromotive force of the given circuit, and inversely proportional to the resistance of the circuit. It also involves the additional truth that in *different parts* of the *same circuit*, where the strength of current is necessarily the same (§ 95), the difference of tension, or potential,* between any two points is always proportional to the resistance between these points.

The third expresses a truth first verified experimentally by Faraday, that the quantity of electricity which passes any point of a circuit, as measured by the amount of electrolysis, is proportional to the strength of the current and the time during which it flows.

The fourth expresses an important law, first demonstrated experimentally by Joule, that the work done by a current (e. g., the quantity of heat generated) is proportional to the square of the current, to the time during which it acts, and to the resistance which it encounters. It should be remembered in this connection that the unit of force acting through one metre does the unit of work; that the force of gravity acting on one gramme of matter through one metre does 9.8 units of work, equal to one metre-gramme; and that the unit of heat (§ 13) is equivalent to 4,157.25 units of work, or 423.8 metre-grammes.

* The influence of the electromotive force extends throughout the circuit, causing at every cross section of the conductor what we may call an *electrical pressure*, which regulates the flow of the electrical current. This pressure is greatest at the surface of the active plate where the power originates, and diminishes as we proceed around the circuit in either direction. At some intermediate section, where the opposite currents neutralize each other, the pressure is zero, and as we move back from this neutral point against the negative current we encounter an ever-increasing "negative" pressure, while in the opposite direction we meet an ever-increasing "positive" pressure. What we here call electrical pressure is called above tension or potential, and without attempting to give a theoretical conception of its nature, it is sufficient to say that it is a force measured at any point of the circuit by the tendency of the current to leave the conductor. Ohm's formula holds not only for the whole circuit, but also for any part of it; but in such cases E stands, not for the whole electromotive force, but for the difference of tension between the two ends of the portion under consideration.

The fifth is involved in the previous three, from which it is readily deduced, and expresses the fact that the work done in any portion of the circuit is proportional to the quantity of electricity which passes over it, and to the difference of tension between the two ends.

100. **Kirchhoff's Laws.** — The following propositions may be deduced from the general theory of electrical currents: —

1st. *The sum of the currents which approach any point is always equal to those which recede from it.*

Or, if we distinguish the first by a plus and the second by a negative sign, we may say more generally, —

The sum of all the currents which meet at a point is equal to zero.

2d. *On any continuous line of conductors the sum of the products of the resistances of the several parts by the strength of the current in each part is equal to the sum of the electromotive forces included in the same closed circuit.*

The last proposition holds true of every circuit which may be traced in any system of conductors and batteries, however complicated the maze; only currents flowing in opposite directions with reference to the given circuit must be distinguished by opposite signs. Moreover, the sum is equal to zero when there is no electromotive force on the line of conductors under consideration.

101. **Electrical Units.** — In the following problems the values C, R, r, and E of Ohm's formula are assumed to be measured in terms of the following units. First, the *unit of current* is that which would produce, by the electrolysis of water, 1 $\overline{\text{c. m.}}^3$ of hydrogen and oxygen gas (measured under standard conditions) in one minute. Secondly, the *unit of resistance* is that offered by a pure silver or copper wire 1 m. long, and 1 m. m. in diameter at 0°. Lastly, the unit of *electromotive force* is that which transmits a *unit current* against a *unit resistance* in a *unit of time*.

By means of the magnetic and thermal relations given by (1) and (4) of § 99 above, it is possible to express the values of the three elements of an electrical current in terms of the funda-

mental units of space, weight, and time, the metre, the gramme, and the second. The following formulæ, in which L = length, M = mass or weight, and T = time, are easily deduced, involving only simple mechanical principles:—

$$\text{Velocity} = V = \frac{L}{T}$$

$$\text{Force} = F = \frac{MV}{T} = \frac{ML}{T^2}$$

$$\text{Work} = W = FL = \frac{ML^2}{T^2}$$

$$\text{Work in metre grammes} = \frac{ML^2}{T^2} \cdot \frac{1}{9.8}$$

$$\text{Strength of pole}^* = m = \frac{L^{\frac{3}{2}}M^{\frac{1}{2}}}{T}$$

$$\text{Strength of current}\dagger = C = \frac{L^{\frac{1}{2}}M^{\frac{1}{2}}}{T}$$

$$\text{Quantity of electricity} = Q = CT = L^{\frac{1}{2}}M^{\frac{1}{2}}$$

$$\text{Electromotive force} = E = \frac{W}{Q} = \frac{M^{\frac{1}{2}}L^{\frac{3}{2}}}{T^2}$$

$$\text{Resistance} = R = \frac{E}{C} = \frac{L}{T} = V$$

The values of C, R, and E, when the several factors in the formulæ expressing their values are each taken equal to unity, are called the electromagnetic units. Thus the unit of resistance is a velocity of one metre a second.‡ These absolute units, however, are of an order of magnitude which is unsuitable for ordinary measurements, but the following very small multiples or submultiples may be used to advantage:—

* This value is readily obtained by considering that the force exerted between the two poles must be $F = \frac{m\,m'}{D^2}$ or $= \frac{m^2}{D^2}$, when the two poles are equal. Hence $m = D\sqrt{F}$.

† Readily derived from value of C, (1).

‡ For the interpretation of this remarkable analytical result, see pamphlet by the author on "Absolute System of Electrical Measurements."

For R the Ohm		equal to 10^9	absolute units of resistance.				
" R " Megohm	"	10^{15}	"	"	"		
" R " Microhm	"	10	"	"	"		
" E " Volt	"	10^8	"	"	electromotive force.		
" E " Megavolt	"	10^{11}	"	"	"	"	
" E " Microvolt	"	10^{-1}	"	"	"	"	
" C " Farad	"	10^{-8}	"	"	quantity per second.		
" C " Megafarad	"	10^{-2}	"	"	"	"	
" C " Microfarad	"	10^{-14}	"	"	"	"	

The unit current is a current of one Farad a second.

A pure copper or silver wire 1 m. m. in diameter and 48.61 metres long has a resistance of one Ohm, at 65° F., and the Committee of the British Association on Electrical Standards have carefully constructed a standard Ohm, of which copies are readily accessible. Further, we have a closely approximate standard of electromotive force in the Daniell cell, which, according to Sir W. Thompson, is equal to 1.079 Volts, or 1 Volt = 0.9268 of force of Daniell cell. One Volt equals about 500.6 of the old units, and a current of one Megafarad per second will yield during one minute by the electrolysis of water 10.3 $\overline{\text{c. m.}}^3$ of gas very nearly.

The admirable instruments now constructed for the purpose enable us to use the B. A. units, as they are called, with great facility; but in solving the following problems the older system will be found more convenient. The student, however, should familiarize himself with both; but he should bear in mind that values in Ohms, Volts, and Farads must be reduced to absolute units before they can be substituted for C, R, or E in Ohm's formula.

QUESTIONS AND PROBLEMS.

1. What resistance does the current suffer in an iron wire 50 metres long and 5 m. m. in diameter? Sp. R. of iron, 7. Ans. 14 units.

2. Assuming that the Sp. R. of copper is 1.3 and that of iron 7, what must be the diameter of an iron wire which will oppose no greater resistance to the current than a copper wire 2 m. m. in diameter? Ans. 4.64 m. m.

3. It is found by experiment that a wire of German silver, 7.201 m. long and 1.5 m. m. in diameter, opposes the same resistance to the current as a wire of pure silver 10 m. long and $\frac{1}{2}$ m. m. in diameter. What is the Sp. R. of German silver? Ans. 12.5.

4. It is required to make, with 132.8 grammes of pure silver, a wire which will offer a resistance of 81 units. What must be its length and diameter? *Sp. Gr.* of silver = 10.57.

Solution. — Representing by x the length in *metres*, and by y the diameter in *millimetres*, we deduce by [1] $y^2 x \frac{\pi}{4} 10.57 = 132.8$, and by the laws of conduction $\frac{x}{y^2} = 81$. Whence $x = 36$ m., and $y = \frac{2}{3}$ m. m.

5. What is the length and diameter of an iron wire weighing 97.38 grammes, which offers a resistance of 9,072 units? It is known that the *Sp. Gr.* of the iron = 7.75 and its Sp. R. = 7.

Ans. Length, 144 m.; diameter, $\frac{1}{3}$ m. m.

6. From a given wire there are four branches, of which the resistance is, respectively, 10, 20, 30, and 40. Required the total resistance when the current passes simultaneously through the four branches.

Solution. — The resistance in the first branch may be represented by a normal silver wire 10 m. long and 1 m. m. in diameter. If we call the area of a transverse section of this wire s, then the resistance in the other three branches will be represented by normal wires of the same length, but having on the cross sections the areas $\frac{1}{2}s$, $\frac{1}{3}s$, and $\frac{1}{4}s$, respectively. If next we conceive of these wires as merged in one, having the common length 10 m. and an area on the section equal to $(1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4})s$, it is evident that such a wire will represent the resistance required. Hence we easily deduce, — Ans. 4.8.

7. A closed circuit has two branches, through which the current passes simultaneously. In one branch $r = 100$. What length of copper wire 5 m. m. in diameter must be used for the other that the total $r = 50$? Ans. 2,500 metres.

8. A conductor has two branches, one having $r = 756$, the other so adjusted that, when the current passes at the same time through both, the *total* resistance equals 540. Required the length of a German silver wire $\frac{1}{2}$ m. m. in diameter and Sp. R. = 12.5, which, when inserted in the adjusted branch, will increase the *total* resistance to 630.

Solution. — By the principle of the last problem we easily find that the resistance in the adjusted branch before insertion equals 1,890, and after insertion, 3,780. The difference between these values, 1,890, is the resistance due to the inserted wire. Hence its length must be 37.8 metres.

9. We have a battery of six Daniell cells, in each of which $E = 475$, $R = 15$, and the external resistance against which the battery is to work, $r = 10$. The cells may be arranged, 1st, as six single elements; 2d, as three double elements;* 3d, as two threefold elements; 4th, as one sixfold element. Required the current strength in each case.

Ans, 28.5, 43.8, 47.5, and 38.0, respectively.

10. We have a battery of twelve Grove cells, in each of which $E = 830$, and $R = 18$, to work against an external resistance of $r = 24$. Required the strength of current when the cells are arranged, 1st, as twelve single; 2d, as six twofold; 3d, as four threefold; 4th, as three fourfold; 5th, as two sixfold; and 6th, as one twelvefold element. Ans. 41.5, 63.8, 69.2, 66.4, 55.3, and 32.5, respectively.

11. With a single cell, where E and R have a constant value, what is the maximum strength of current, and under what conditions would it be obtained?

Ans. $\frac{E}{R}$, when the external resistance is nothing.

12. With n cells, in each of which E and R have the same value, what is the maximum strength of current, and under what conditions would it be obtained?

Ans. $n\frac{E}{R}$, when the cells are arranged as one n-fold element, and work against no external resistance.

13. With n cells, as above, working against a given external resistance r, how should they be arranged so as to obtain the maximum value of C?

Ans. So as to make the internal resistance equal to that of the external circuit.

* By double elements is meant a group of two cells coupled for quantity (§ 96) and equivalent to a large cell having plates of twice the size. Six double elements are six such groups arranged for intensity, and the other terms have a similar meaning.

Solution. — If x represents the number of compound elements formed with the n cells when C in Ohm's formula is a maximum, we should evidently have under this condition x compound elements, each formed of $\frac{n}{x}$ cells. The electromotive force of such an arrangement would be xE. The internal resistance would be $xR \div \frac{n}{x} = \frac{x^2}{n} R$ (compare Problems 8 and 9), and the strength of the maximum current required,

$$C = \frac{xE}{\frac{x^2}{n} R + r}.$$

The first differential coefficient [illegible] is function of x when C is a maximum must be equal to zero. [illegible]

$$\frac{\quad}{\quad} = \frac{\frac{x^2}{n} RE}{\quad} = 0,$$

$$\left(\frac{2}{n} E + \right.$$

or

[illegible]

That is, the strength of the current is at its maximum when the internal equals the external resistance, as stated above. Those who are not familiar with the elementary principles of the differential calculus may satisfy themselves of the truth of this result by comparing the answers obtained to Problems 8 and 9.

14. We have, in the first place, for a single cell of a given combination working against a fixable resistance, the value $C = \frac{E}{R + r}$; in the second place, for n cells of the same combination working against n times the resistance, the identical value $C = \frac{nE}{nR + nr}$. In strength the two currents are equal, but are they identical?

15. In a given cell $E = 1.5$; $R = 1.5$. The current passes through 30 metres of pure copper wire 2 m. m. in diameter. It is required to arrange 8 cells so that C may be the greatest possible.

Ans. They should be arranged as two fourfold elements.

16. We have a battery of four Bunsen cells ($E = 1.8$, $R = 4$ each) coupled as four simple elements. The circuit is closed through 500

grammes of pure copper wire. Required the greatest strength of current, and the dimensions of the wire, that this maximum may be obtained.

17. A simple Voltaic cell, whose electromotive force, E, is known, working against an unknown total resistance R' (both external and internal), produces a given effect upon a galvanometer. Another cell differently constructed, working against a total resistance R'', also unknown, produces the *same* effect upon the galvanometer. It is also observed that a measured length, l, of normal copper wire, inserted in the first circuit, produces on the galvanometer the same difference of effect as a length, l', inserted in the second circuit. Required the electromotive force, E', of the second cell.

Solution. — We easily deduce from Ohm's formula the two equations $\frac{E}{R'} = \frac{E'}{R''}$ and $\frac{E}{R' + l} = \frac{E'}{R'' + l'}$, whence we obtain, —

Ans. $E' = E\frac{l'}{l}$.

18. In order to determine the electromotive force of a Bunsen cell, it was compared, as in the last problem, with a Daniell cell whose electromotive force was known to be 470. After adjusting the external resistances so that both produced the same effect upon the galvanometer, it was found that the insertion of 5.6 m. of copper wire into the first circuit caused the same change in the instrument as the insertion of 3.29 metres of the same wire in the circuit of the Daniell cell. What was the electromotive force sought? Ans. 800.

19. A battery of 40 Bunsen cells remains closed for an hour, and during that time furnishes a current whose strength $C = 30$. How much zinc will be consumed in this time, assuming that there is no local action?

Solution. — Such a current would produce, by the electrolysis of water, 30 $\overline{\text{c. m.}}^3$ of gas in one minute, or 1.8 litres in one hour. Of this gas 1.2 litres or 1.2 criths would be hydrogen. The chemical equivalent of zinc being 32.6, the amount of zinc dissolved in each cell must be $1.2 \times 32.6 = 39.12$ criths, and in the 40 cells, 1,564.8 criths, equal to 140 grammes, the answer required.

20. In an electrotype apparatus (Fig. 20) 16.36 grammes of copper were deposited on the negative mould in 24 hours. What was the strength of current? Ans. 6 units.

21. In an electrotype apparatus the electromotive force of the single cell employed is 420, and the internal resistance 5. The external resistance, including decomposing cell, is 0.25. How much copper will be deposited on the negative mould in one hour, and how much zinc will be dissolved in the battery during the same time?

Ans. 9.088 grammes of copper and 9.346 grammes of zinc.

22. Thirty-two Grove cells ($E = 830$, $R = 20$ each) are connected as 4 eightfold compound elements, and the current employed to work an electro-silvering apparatus, in which the total resistance external to the battery was equivalent to 10. Required the number of grammes of silver deposited each hour, and the number of grammes of zinc dissolved during the same time in the battery.

Ans. 64.24 grammes of silver and 77.56 grammes of zinc.

23. Assuming that the external resistance cannot be changed, could the same number of cells of the battery described in the last problem be so arranged as to deposit more silver in the same time?

Ans. They could not.

Could they be so arranged as to deposit the same amount of silver with less expense of zinc? What would be the most economical arrangement, and under these conditions how much silver would be deposited in one hour, and how much zinc dissolved?

Answer to the last question, 30.25 grammes of silver and 9.13 grammes of zinc.

24. What is the current through 25 Ohms with a tension of 5 Volts?

Ans. $C = \frac{E}{R} = \frac{5 \times 10^8}{25 \times 10^7} = 0.5 \times 10^{-1}$, or 0.5 Megafarad.

25. What is the work done by a current of 5 Megafarads per second through a resistance of 10 Ohms?

Ans. $W = C^2Rt = (5 \times 10^{-7})^2 \times 10 \times 10^7 = 250{,}000$ units per second.

26. What is the work done by 1,000 Farads in falling in tension 1 Volt?

Ans. $W = QE = 1{,}000 \times 10^{-8} \times 10^5 = 1{,}000 \times 10^{-3} = 1$ unit of work. Hence 9,800 Voltfarads equal 1 metre-gramme.

27. What would be the answers to Problem 10 in B. A. units? Assuming that nine tenths of the external resistance is in a coil of

platinum wire surrounded by a kilogramme of water, how high would the temperature of the water be raised in ten minutes?

28. Assuming that in the system of conductors represented in Fig. 21, E represents the electromotive force of the voltaic element, R the total resistance of the main conductor $a\,E\,b$, R_1 and R_2 the resistances of the two conductors into which the main stream divides, find the values of the three corresponding currents C, C_1, and C_2, in terms of E, R, R_1, and R_2. Prove also that $C_1 : C_2 = R_2 : R_1$, and further, that $C_1 = C\,\frac{R_2}{R_1 + R_2}$ or $C_2 = C\,\frac{R_1}{R_1 + R_2}$. Lastly, show that the equivalent resistance of any number of branches may be found by adding together the reciprocals of each branch and taking the reciprocal of this sum. A conductor like R_2, which diverts a portion of the main current from R_1, is called a shunt, and if R_1 is the coil of a galvanometer, the galvanometer would be said to be shunted by R_2, and by adjusting the value of R_2 to R_1 we can cause a known fraction of the whole current to pass through the instrument.

Fig. 21.

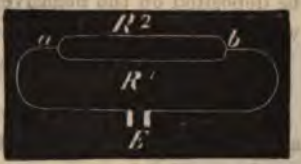


Fig. 22.

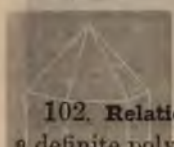
29. In the system of conductors represented in Fig. 22, called Wheatstone's bridge, no current passes over the bridge between c and d when $R_1 : R_2 = R_3 : R_4$. Prove the truth of this proposition, and show how it may be applied for measuring resistances when we have a set of standard resistance coils.

Fig. 23.

30. In the system of conductors, represented in Fig. 23, prove that no current passes in the portion $a\,E'\,b$ when $\frac{E'}{E} = \frac{R_0}{R + R_0}$, and consider how the system may be used for comparing the electromotive force of different cells.

CHAPTER XVI.

CRYSTALLINE FORMS.



102. **Relations to Chemistry.** — Almost every substance affects a definite polyhedral form, although it may manifest this tendency only under favorable conditions. Such forms are called crystals, and the process of crystalline growth, or development, is called crystallization. The one essential condition of crystallization is a certain freedom of motion, and crystals, more or less perfect, are usually formed whenever a molten liquid "sets," or a solid is deposited from a condition of solution or of vapor; and in each case, the slower the process, the larger and the more perfect are the crystals. The crystalline condition is, in fact, the normal state of solid matter. It is true that there are a few substances which, like glue, are only known in the colloid state; but in most of the so-called colloid substances this state is abnormal, and there is a constant tendency to crystallization. Moreover, its peculiar crystalline form is one of the most characteristic, and apparently one of the most essential, properties of a substance, and is therefore of great value in determining its chemical affinities. The study of the geometrical relations of these forms is, however, in itself a separate science, and in this connection we can only dwell on the few elementary principles of the subject on which our system of chemical classification in part rests.

103. **Definitions.** — In the forms of crystals the idea of symmetry is the great controlling principle. Each substance follows a certain law of symmetry, which seems to be inherent, and a part of its very nature; and when from any cause the character of the symmetry changes, the substance loses its identity, and, even if its chemical composition remains the same, it becomes, to all intents and purposes, a different substance. In every crystal the symmetry points to a few *directions*, to which not only the position of the planes, but also the physical properties

of the body, are closely related. Certain of these *directions*, more or less arbitrarily chosen, are called the *axes* of the crystals, and a *crystalline form* may be defined as a group of *similar* planes symmetrically disposed around these axes. As is evident from this definition, a crystalline form, like a geometrical form, is a pure abstraction, and this conception is carefully to be kept distinct from the idea of a crystal, which implies not only a certain form, but also a certain structure. Moreover, in by far the larger number of cases the same crystal is bounded by several forms. Thus, in Fig. 24, which represents a crystal of common quartz, the planes of the prism and the planes of the pyramid are distinct crystalline forms.

Fig. 24.

104. **Systems of Crystals.** — A careful study of the forms of crystals has shown that these forms may be classified under six crystalline systems, each of which is distinguished by a peculiar plan of symmetry. These divisions, it is true, are in a measure arbitrary, for here, as elsewhere in nature, no sharp dividing lines are found; but nevertheless the distinctions on which the classification rests are clearly marked. We can only give in this book a very imperfect idea of these several plans of symmetry by representing with figures a few of the more characteristic forms of each.

105. **First, or Isometric System.*** — The three most frequently occurring forms of this system are the regular octahedron, the

Fig. 25.

Fig. 26.

Fig. 27.

rhombic dodecahedron, and the cube (Figs. 25, 26, and 27). These and all the other forms of the system may be regarded as grouped

* Called also monometric.

around three equal and similar axes at right angles to each other, and hence the name *isometric* (equal dimensions). They present the same symmetry on all sides, and the appearance of the form is identical, whichever axis is placed in a vertical position. In this system no variation in the relative positions or lengths of the axes is possible, for this would change the plan of symmetry on which the system is based.

106. **Second, or Tetragonal System.*** — The plan of symmetry in this system is best illustrated by the square octahedron (Fig. 28). Of this form the basal section (Fig. 29) is a square, and to this fact

Fig. 28.

Fig. 29.

Fig. 30.

the name of the system refers. The vertical section, on the other hand, is a rhomb (Fig. 30). Here, as in the first system, the forms may all be referred to three rectangular axes, but only two have the same length; the third may be either longer or shorter than the others. The last is the dominant axis of the form, and hence we always place it in a vertical position, and call it the vertical axis. The length of the vertical axis bears a constant ratio to that of the lateral axes in all crystals of the

Fig. 31.

Fig. 32.

same substance, but this ratio differs very greatly for different substances, and is therefore an important crystallographic character. The familiar square prism is another very characteristic form of this system.

* Called also dimetric.

Moreover, the planes both of the prism and of the octahedron may have different positions with reference to the lateral axes, as is shown by the two basal sections (Figs. 31 and 32); and this leads us to distinguish two square prisms and two square octahedrons, one of which is said to be the inverse of the other.

107. **Third, or Hexagonal System.** — In the last system the planes were arranged by fours around one dominant axis, while in this system they are arranged by sixes. The most characteristic forms of this system are the hexagonal pyramid (Fig. 33),

Fig. 33.

Fig. 34.

Fig. 35.

and the hexagonal prism (Fig. 34). The basal section through either of these forms is a regular hexagon (Fig. 35), and, besides the dominant or vertical axis, we also distinguish as lateral axes the three diagonals of this hexagonal section. These lateral axes stand at right angles to the vertical axis, but between themselves they subtend angles of 60°. Here, as before, the ratio of the length of the vertical axis to the common length of the lateral axes has a constant value on crystals of the same sub-

Fig. 36.

Fig. 37.

stance, but differs very greatly with different substances, the vertical axis being sometimes longer and sometimes shorter than

the other three. The rhombohedron (Fig. 36) and the scalenohedron (Fig. 37) are also forms of this system, and occur even more frequently than the more typical forms first mentioned. Lastly, a difference of position in the planes of the prism or pyramid with reference to the lateral axes gives rise in this system to the same distinction between the direct and the inverse forms as in the last.

108. **Fourth, or Orthorhombic System.*** — The most characteristic forms of this system are the rhombic octahedron (Fig. 38) and the right rhombic prism, from which the system takes its name. The three principal sections of the octahedron, represented by Figs. 39, 40, and 41, and also the basal section of the

Fig. 38.

Fig. 39.

Fig. 40.

Fig. 41.

prism, are all rhombs, whose relations to the form are indicated by the lettering of the figures. We easily distinguish here three axes at right angles to each other, but of unequal lengths, and in regard to the ratios of these lengths the remarks of the last two sections are strictly applicable.

109. **Fifth, or Monoclinic System.** — The forms classed together under this system may be referred to three unequal axes, one of which stands at right angles to the *plane* of the other two, while they are inclined to each other at an angle which, though constant on crystals of the same substance, varies very greatly with different substances, as vary also the relative dimensions of the axes themselves. Fig. 42 represents an octahedron of this system, and Figs. 43 and 44 represent two sections made through the edges *FF* and *DD'* of this form. A section through the edges

* Called also trimetric.

CC would be similar to Fig. 43, and these three sections give a clear idea of the relative positions of the axes. The section (Fig. 44) containing the two oblique axes is called the plane of symmetry, and the faces on all monoclinic crystals are disposed symmetrically solely with reference to this plane. In a word,

Fig. 42.

Fig. 43.

Fig. 44.

the symmetry is bilateral, and corresponds to the type with which we are so familiar in the structure of the human body. This plan of symmetry is well illustrated by Figs. 45, 46, and 47, which represent the commonly occurring forms of gypsum, augite, and felspar, three of the most common minerals. These figures, however, do not, like those of the previous sections, represent simple crystalline forms. The crystals here represented are in each case bounded by several forms, and indeed in this system such compound forms are alone possible, for no simple monoclinic form can of itself enclose space.

Fig. 45.

Fig. 46.

Fig. 47.

110. **Sixth, or Triclinic System.** — This system is distinguished by an almost complete want of symmetry. Only opposite planes are similar, and two such planes constitute a complete crystalline form. Hence on every crystal there must be at least three simple forms. We may refer the planes of any crystal to

Fig. 48.

three unequal axes all oblique to each other, but the position we assign to them is quite arbitrary, and they have therefore little value as crystallographic elements. Fig. 48 represents a crystal of sulphate of copper, one of the very few substances which crystallize in this system.

111. **Modifications on Crystals.** — When several crystalline forms appear on the same crystal, some one is usually more prominent or *dominant* than the rest, and gives to the crystal its general aspect, the planes of the secondary forms only appearing on its edges or solid angles, which are then said to be modified or replaced. Thus, in Figs. 49, 50, and 51, the solid angles of a cube are replaced (or truncated) by the faces of an octahedron; in Fig. 52 the edges of the cube are replaced by the faces of the dodecahedron; in Fig. 53 the edges of the octahedron are modified in the same way; and in Fig. 54 the solid angles of a dodecahedron are replaced by the faces of an octahedron. These

Fig. 49.

Fig. 50.

Fig. 51.

Fig. 52.

Fig. 53.

Fig. 54.

are all forms of the isometric system; and the relations of the simple forms to each other, which determine in every case the position of the secondary planes, will be readily seen on comparing together the figures already given on page 245. These figures, like all crystallographic drawings, are geometrical projections, and represent the planes in the same relative position towards the

crystalline axes which they have on the crystal itself. Moreover, since in all figures of crystals of this system the axes are drawn in absolutely the same position on the plane of the paper, the same face has also the same position throughout.

Fig. 55.

Fig. 56.

Fig. 57.

Fig. 58.

As a general rule, *all the similar parts of a crystal are simultaneously and similarly modified.* This important law, which is

Fig. 59.

Fig. 60.

Fig. 61.

a simple inference from the principles already stated, is illustrated by the figures just given, and also by Figs. 55 to 70. By carefully

Fig. 62.

Fig. 63.

Fig. 64.

studying these figures, as well as Figs. 45 to 48 on pages 249, 250, the student will be able to refer each of the compound crys-

tals here represented to one of the several systems of symmetry already described, and from this and similar practice he will learn, better than from any descriptions, how clearly the modifications on a crystal point out its crystallographic relations.

112. **Hemihedral Forms.** — To the law governing the modifications of crystals just stated, there is one important exception.

Fig. 65. Fig. 66. Fig. 67. Fig. 68.

It not unfrequently happens that *half the similar parts of a crystal are modified independently of the other half.* Thus in

Fig. 69. Fig. 70.

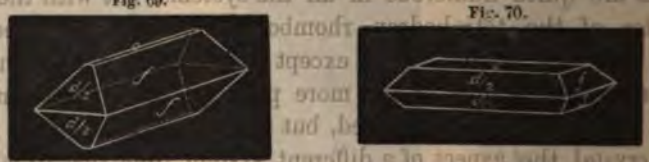


Fig. 71 only one half of the solid angles of the cube are truncated. The modifying form in this case is the tetrahedron (Fig. 73),

Fig. 71. Fig. 72. Fig. 73.

also a simple form of the isometric system. When all the solid angles of the cube are truncated, the modifying form, as has

been shown, is the octahedron, and the relation which the tetrahedron bears to the octahedron is shown by Fig. 72. The rhombohedron (Fig. 74) stands in a similar relation to the hexagonal pyramid (Fig. 75). From these figures it is evident that, while the octahedron and the hexagonal pyramid have all the planes which perfect symmetry requires, the tetrahedron and the rhombohedron have only half the number, and in crystallography all forms which bear a similar relation to the forms of perfect symmetry are said to be *hemi*hedral, while the forms of perfect symmetry are distinguished as *holo*hedral. The hemihedral forms are quite numerous in all the systems, but with the exception of the tetrahedron, rhombohedron, and scalenohedron (Fig. 37), they seldom appear except as modifying planes on the edges or solid angles of the more perfect forms. As a general rule, they are easily recognized, but not unfrequently they give to a crystal the aspect of a different system from that to which it really belongs, and may lead to false inferences; but these can, in most cases, be corrected by a careful study of the interfacial angles.

Fig. 74.

Fig. 75.

113. **Identity of Crystalline Form.** — As has already been stated, every substance is marked by certain peculiarities of outward form, which are among its most essential qualities, and we must next learn in what these peculiarities consist. As a general rule, the same substance crystallizes in the same form, but under unusual circumstances it frequently appears in other forms of the same system. Thus fluor-spar is usually found crystallized in cubes, but in large collections crystals of this mineral may be seen in almost all the holohedral forms of the isometric system, including their numerous combinations. In like manner common

salt usually crystallizes in cubes, but out of a solution containing urea it frequently crystallizes in octahedrons. Moreover, the same principle holds true in regard to substances crystallizing in other systems, most of whose forms never appear except in combination. Thus the mineral quartz generally shows the simple combination represented in Fig. 24; but more than one hundred other forms — all, however, belonging to the same system — have been observed on crystals of this well-known substance. So also the crystals of gypsum, augite, and felspar in most cases present the forms already figured on page 249, although other forms are common, which, however, all belong to the same crystalline system. We never find the same substance in the forms of different systems except in those cases of polymorphism already described (page 139), where the differences in other properties are so great that the bodies can no longer be regarded as the same substance.

Among substances crystallizing in the isometric system the crystalline form is not so distinctive a character as it is in other cases. In this system the relative dimensions are invariable, and the octahedron, the dodecahedron, and the cube, more or less modified by different replacements, are the constantly recurring forms. Even here, however, specific differences may at times be found in the fact that some substances affect hemihedral forms on modification, while others do not. In all the other systems the dimensions of the crystal (the relative lengths of its axes and the values of the interaxial angles) distinguish each substance from every other. But here, also, the general statement must be somewhat modified.

Fig. 76.

We frequently find on the crystals of the same substance several forms having different axial dimensions. Thus, on the crystal represented by Fig. 76, belonging to the tetragonal system, there are three different octahedrons, and three corresponding values of the vertical axis. But if, beginning with the planes of the octahedron O, we determine the ratio which its vertical axis bears to the common length of the two lateral axes, and call this value a, we shall

find that the corresponding values for the two other octahedrons are $2a$ and $\frac{1}{2}a$, respectively. Moreover, if we extend our study we shall also find that this example illustrates a general principle, and that *the crystalline forms of a given substance include, not only those of identical axial dimensions, but also those whose dimensions bear to each other some simple ratio.*

This most important law gives to the science of crystallography a mathematical basis, and enables us to apply the exhaustive methods of analytical geometry in discussing the various relations of the subject. Among the actual forms of a given substance we fix on some one as the fundamental form, and, taking the values of its axial dimensions as our standards, we are able to express the position of the planes of all the possible forms by means of very simple symbols, and also to express by mathematical formulæ the relations of the interfacial angles to the same fundamental elements of the crystal; so that the one may readily be calculated from the other.

It may seem at first sight that the crystallographic distinction between different substances, insisted on above, is greatly obscured by the important limitations just made. But it is not so, at least to any great extent. The selection of the fundamental form of a given substance is not arbitrary, although it is based on considerations which it lies beyond the scope of this book to discuss. Moreover, an error in this choice is not fundamental, since the true conception of the form of a substance includes not only the fundamental form, but all those which are related to it. This conception, though not readily embodied in ordinary language, is easily expressed by a general mathematical formula, and is as clear to one familiar with the subject as the general statement first made.

But, however obscure to those who are not familiar with mathematical conceptions may be the distinction between the forms of different substances in the same system, the difference between the different systems is clear and definite, and it is with this broad distinction that we have chiefly to deal in our chemical classification.

114. **Irregularities of Crystals.** — It must not be supposed that

natural crystals have the same perfection of form and regularity of outline which our figures might seem to indicate. In addition

Fig. 77.

Fig. 78.

Fig. 79.

to being more or less bruised or broken from accidental causes, crystals are rarely terminated on all sides, — one or more of the

Fig. 80.

Fig. 81.

faces being obliterated where the crystal is implanted on the rock, or where it is merged in other crystals. But by far the most

Fig. 82.

Fig. 83.

remarkable phase which the irregularities of crystals present is that shown by Figs. 77 to 87. By comparing together the figures

which have been here grouped together on these pages, and which represent in each case different phases of the same crystalline form, it will be seen that the variations from the normal type are caused by the undue development of certain planes at the expense of their neighbors, or by an abnormal growth of the crystal in some one direction.

Such forms as these, however, although great departures from the ideal geometrical types, are in perfect harmony with the principles of crystallography. The axis of a crystal is not a definite line, but a definite direction; and the face of a crystal is not a plane of definite size, but simply an extension in two definite directions. These directions are the only fundamental elements of a crystalline form, and they are preserved under all

Fig. 84.

Fig. 85.

Fig. 86.

Fig. 87.

conditions, as is proved by the constancy of the interfacial angles, and of the modifications, on crystals of the same substance, however irregular may have been the development.

115. **Twin Crystals.** — Every crystal appears to grow by the slow accretion of material around some nucleus, which is usually a molecule or a group of molecules of the same substance, and which we may call the crystalline molecule or germ. Now we must suppose that these molecules have the same differences on different sides which we see in the fully developed crystal, and which, for the want of a better term, we may call *polarity*. As a general rule, in the aggregation of the molecules a perfect parallelism of all the similar parts is preserved. But if molecular polarity at all resembles magnetic polarity, it may well be that two crystalline molecules might become attached to each

other in a reversed position, or in some other definite position determined by the action of the polar forces. Assume now that each of these crystalline molecules "germinates," and the result would be such twin crystals as we actually find in nature. The result is usually the same as if a crystal of the normal form

Fig. 88.

Fig. 89.

Fig. 90.

Fig. 91.

were cut in two by a plane having a definite position towards the crystalline axes, and one part turned half round on the other; and twins of this kind are therefore called hemitropes (Figs. 88 to 91). At other times the germinal molecules seem to have become attached with their dominant axes at right

Fig. 92.

Fig. 93.

angles to each other, and then there result twins such as are represented in Figs. 92 and 93; and many other modes of twinning are possible. Some substances are much more prone to the formation of twin crystals than others, and the same substance generally affects the same mode of twinning, which may thus become an important specific character. The plane which separates the two members of a twin crystal, called the plane of twinning, has always a definite position, and is in every case

parallel either to an actual or to a possible face on both of the two forms.

Twin crystals always preserve the same symmetry of grouping, and the values of the interfacial angles between the two forms are constant on crystals of the same substance, so that they might sometimes be mistaken for simple crystals by unpractised observers. There is, however, a simple criterion by which they can be generally distinguished. Simple crystals never have re-entering angles, and, whenever these occur, the faces which subtend them must belong to two individuals.

The same principle which leads to the formation of twin crystals may determine the grouping of several germinal molecules, and lead to the formation of far more complex combinations. Frequently, as it would seem, a large number of molecules arrange themselves in a line, with their principal axes parallel and their dissimilar ends together, and hence result linear groups of crystals alternating in position, but so fused into each other as to leave no evidence of the composite character except the re-entering angles, and frequently these are marked only by the striations on the surface of the resulting faces. Such a structure is peculiar to certain minerals, and the resulting striation frequently serves as an important means of distinction. The orthoclase and the klinoclase felspars are distinguished in this way.

116. **Crystalline Structure.** — The crystalline form of a body is only one of the manifestations of its crystalline structure. This also appears in various physical properties, which are frequently of great value in fixing the crystallographic relations of a substance, and such is especially the case when, on account of the imperfection of the crystals, the crystalline form is obscure. Of these physical qualities one of the most important is *cleavage*.

As a general rule, crystallized bodies may be split more or less readily in certain definite directions, called planes of cleavage, which are always parallel either to an actual or to a possible face on the crystals of the substance, and are thus intimately associated with its crystalline structure. At times the cleavage is very easily obtained, when it is said to be *eminent*, as in the case of mica or gypsum, which can readily be split into exceed-

ingly thin leaves, while in other cases it can only be effected by using some sharp tool, and applying considerable mechanical force. With a few unimportant exceptions the cleavage planes have the same position on all specimens of the same substance. Thus specimens of fluor-spar may be readily cleaved parallel to the faces of an octahedron (Fig. 25), those of galena parallel to the faces of a cube (Fig. 27), those of blende parallel to the faces of a dodecahedron (Fig. 26), and those of calc-spar parallel to the faces of a rhombohedron (Fig. 36). In these cases, and in many others, the cleavage is a more distinctive character than the external form, and can be more frequently observed, and we generally regard the form produced by the union of the several planes of cleavage as the fundamental form of the substance.

Again, we always find that cleavage is obtained with equal ease or difficulty parallel to similar faces, and with unequal ease or difficulty parallel to dissimilar faces. Moreover, the dissimilar cleavage faces thus obtained may generally be distinguished from each other by differences of lustre, striation, and other physical characters; and such distinctions are frequently a great help in studying the crystallographic relations of a substance. Similar differences on the natural faces of crystals are also equally valuable guides.

But of all the modes of investigating the crystalline structure of a body, none can compare in efficiency with the use of polarized light. It is impossible to explain the theory of this beautiful application of the principles of optics without extending this chapter to a length wholly incompatible with the design of this book. It must suffice to say, that, if we examine with a polarizing microscope a thin slice of any transparent crystal of either the second or third system, cut parallel to the dominant axis, we see a series of colored rings, intersected by a black cross, and it is evident that the circular form of the rings answers to the perfect symmetry which exists in these systems around the vertical axis. If, however, we examine in a similar way a slice from a crystal of one of the last three systems, cut in a definite direction, which depends on the molecular structure and must be found by trial, we see a series of oval rings with two distinct

centres, indicating that the symmetry is of a different type. Moreover, the distribution of the colors around the two centres corresponds in each case to the peculiarities of the molecular structure, and enables us to decide to which of the three systems the crystal belongs.

The use of polarized light has revealed remarkable differences of structure in different crystals of the same substance, connected with the hemihedral modifications described above. Figures 94 and 96 represent crystals of two varieties of tartaric acid, which

Fig. 94.

Fig. 95.

Fig. 96.

only differ from each other in the position of two hemihedral planes, and are so related that, when placed before a mirror, the image of one will be the exact representation of the other. The intermediate Figure 95 represents the same crystal without these modifications. Since the solid angles are all similar, we should expect to find them all modified simultaneously; but while on crystals of common tartaric acid only the two front angles (as the figure is drawn) are replaced, a variety of this acid has been discovered having similar crystals whose back angles only are modified. Now it is found that a solution of the common acid rotates the plane of polarization of a beam of light to the right, while a similar solution of this remarkable variety rotates the plane of polarization to the left. This difference of crystalline structure, moreover, is associated with certain small differences in the chemical qualities of the two bodies; but the difference is so slight that we cannot but regard them as essentially the same substance, and the polarized light thus reveals to

us the beginnings of a difference of structure, which, when more developed, manifests itself in the phenomena of isomerism. It is a remarkable fact, worthy of notice in this connection, that these two varieties of tartaric acid chemically combine with each other, forming a new substance called racemic acid.

QUESTIONS.

1. By what peculiar mode of symmetry may each of the six crystalline systems be distinguished? How may crystals belonging to the first system be recognized? How may crystals of the second, third, and fourth systems be distinguished by studying the distribution of the similar planes around their terminations or dominant axes? By what peculiar distribution of similar planes may the crystals of the fifth and sixth systems be distinguished from all others? State the system to which each of the crystals, represented by the various figures of this chapter, belongs, and give the reason of your answer in every case.

2. We find in the mineral kingdom two different octahedral forms of titanic acid belonging to the tetragonal system. In one of these forms the ratio of the unequal axes is 1 : 0.6442, in the other it is 1 : 1.7723. Can these forms belong to the same mineral substance?

CHAPTER XVII.

CHEMICAL CLASSIFICATION.

117. **General Principles.** — The glimpses that we have been able to gain of the order in the constitution of matter give us grounds for believing that there is a unity of plan pervading the whole scheme, and encourage a confident expectation that hereafter, when our knowledge becomes more complete, we may attain to at least such a partial conception of this plan as will enable us to classify all substances under some natural system; and in imagination we may even look forward to the time when science will be able to express all the possibilities of this scheme with a few general formulæ, by which we can predict with absolute certainty the qualities and relations of any given combination of materials or conditions. But although to a very slight extent the idea has been realized for a small class of the compounds of carbon, yet as a whole this grand conception is only a dream. The more advanced student will find that in limited portions of some few fields of investigation a fragmentary classification is possible, as in mineralogy; but when he attempts to comprehend the whole domain, he becomes painfully aware of the immense deficiencies of his knowledge, he is confused by the numerous chains of relationship, which he follows, with no result, to sudden breaks, and soon becomes convinced that all such efforts must be fruitless until more of the missing links are supplied.

The best that can now be done in an elementary treatise on chemistry is to group together the elements, or rather the elementary atoms, in such families as will best show their natural affinities; and then to study, under the head of each element, the more important and characteristic of its compounds. However little value such a classification may have in its scientific aspect, it will bring together, to a greater or less extent, the

allied facts of the science, and thus will help the mind to retain them in the memory.

In classifying the elementary atoms, the three most important characters to be observed are the *Prevailing Quantivalence*, the *Electrical Affinities*, and the *Crystalline Relations*. The first of these characters serves more particularly to classify the elements in groups, the second to determine their position in the groups, and the last to control the indications of the other two. The crystalline relations of the atoms can only be determined by comparing the crystalline forms of allied compounds, and involve the principles of isomorphism already discussed. More trustworthy inferences as to the crystalline relations may be drawn from the crystalline form and properties of allied compounds, than from those of the elementary substances; for, in addition to the fact that so many of these substances crystallize in the isometric system, whose dimensions admit of no variation, it is also true that, in our ignorance of the molecular constitution of most of them, we often have more certainty, in the case of compounds, that our comparisons are made under identical molecular conditions.

118. **Metallic and Non-Metallic Elements.** — In all works on chemistry since the time of Lavoisier, the elementary substances have been divided into two great classes, — the *metals* and the *non-metals;* and the distinction is undoubtedly fundamental, although too much importance has been frequently attached to the accident of a brilliant lustre. The characteristic qualities of a metal, with which every one is more or less familiar, are the so-called *metallic lustre*, that peculiar adaptability of molecular structure known as *malleability* or *ductility*, and the *power of conducting electricity or heat*. These qualities are found united and in their perfection only in the true metals, although one or even two of them are well developed in several elementary substances which, on account of their chemical qualities, are now almost invariably classed with the non-metals, — as, for example, in selenium, tellurium, arsenic, antimony, boron, and silicon. Besides the properties above named, many persons also associate with the idea of a metal a high specific gravity; but this prop-

erty, though common to most of the useful metals, is by no means universal; and among the metals with which the chemist is familiar we find the lightest as well as the heaviest of solids. The non-metallic elements, as the name denotes, are distinguished by the absence of metallic qualities; but the one class merges into the other.

The presence or absence of metallic qualities in the elementary substances is for some unknown reason intimately associated with the electrical relations of their atoms, — those of the metals being electro-positive, while those of the non-metals are electro-negative, with reference, in each case, to the atoms of the opposite class. Indeed, these electrical relations were formerly made the chief basis of classification, and in the older works on chemistry a list of the elementary substances is frequently given, arranged in such an order that each is electro-positive to all which precede it, and electro-negative to all which follow it in the series. Such a classification, however, does not exhibit the other affinities of the elements, and has little practical value.

119. **Periodic Law.** — If the chemical elements are arranged as on the next page, in the order of their atomic weights, it will be seen that those having similar properties and relations recur at nearly regular intervals. Take, for example, the alkaline metals, sodium, potassium, rubidium, and cæsium, which form a well-marked family among the elementary substances, and notice the position which the members of this family have in the table, and it will appear that they are distributed quite regularly through the list. Compare now the position of these elements with those of four other well-marked families; — first, fluorine, chlorine, bromine, and iodine; secondly, oxygen, sulphur, selenium, and tellurium; thirdly, nitrogen, phosphorus, arsenic, and antimony; fourthly, magnesium, calcium, strontium, and barium; — and the very remarkable alternations will be at once manifest, and what we mean by a periodic law will become evident. If now we arrange the elements, as has been done on page 267, still in the order of their atomic weights, but in horizontal lines, beginning a new line as soon as a period is obviously ended, and an element recurs allied to one of those which have preceded, we

ELEMENTS.

IN THE ORDER OF THEIR ATOMIC WEIGHTS.

Name.	Atomic Weight.	Name.	Atomic Weight.	Name.	Atomic Weight.
Hydrogen	1.	Cobalt	58.	Uranium	120.
Lithium	7.	Nickel	58.	Antimony	120.
Boron	11.	Copper	63.	Iodine	126.8
Carbon	12.	Zinc	65.2	Tellurium	128.
Glucinum	13.9	Gallium	70.	Cæsium	133.
Nitrogen	14.	Arsenic	75.	Barium	137.1
Oxygen	16.	Selenium	79.2	Cerium	141.
Fluorine	19.	Bromine	80.	Lanthanum	139.
Sodium	23.	Rubidium	85.4	Didymium	140.
Magnesium	24.	Strontium	87.6	Erbium	167.
Aluminum	27.	Zirconium	89.6	Tantalum	182.
Silicon	28.	Columbium	94.	Tungsten	184.
Phosphorus	31.	Ytterbium	173.	Gold	197.
Sulphur	32.	Molybdenum	96.	Platinum	194.8
Chlorine	35.5	Rhodium	104.4	Iridium	192.7
Potassium	39.1	Ruthenium	104.4	Osmium	199.2
Calcium	40.	Palladium	106.6	Mercury	200.
Titanium	50.	Silver	108.	Thallium	204.1
Vanadium	51.3	Cadmium	112.	Lead	206.9
Chromium	52.2	Indium	113.7	Bismuth	210.
Manganese	55.	Tin	118.	Thorium	231.4
Iron	56.				

shall bring the members of each of the well-marked families of elements we have indicated into one of the vertical columns thus formed, and at the same time associate in the other vertical columns elements which are more or less closely allied. Here, as in most classifications, more or less humoring is required in order to exhibit the relationship of the elements to the best advantage, and, with a single exception, each of the eight primary columns is divided into two or more parallel columns for this purpose. The members of these subordinate series are more or less affiliated, but not closely allied.

The details of this classification cannot be discussed intelligently until the student is familiar with the properties and

TABLE OF THE NATURAL ARRANGEMENT OF THE ELEMENTS.

I.			II.		III.				IV.	V.		VI.		VII.		VIII.		
Hydrogen 1	Lithium 7.01	—	Glucinum 9.2	—	Boron 11	—	—	—	Carbon 11.97	Nitrogen 14.01	—	Oxygen 15.96	—	Fluorine 19.1	—	—	—	—
—	Sodium 22.99	—	Magnesium 23.94	—	Aluminum 27.3	—	—	—	Silicon 28	Phosphorus 30.96	—	Sulphur 31.98	—	Chlorine 35.37	—	—	—	—
—	Potassium 39.04	—	—	Calcium 39.90	—	—	—	—	Titanium 48	—	Vanadium 51.2	—	Chromium 52.4	—	Manganese 54.8	Iron 55.9	Nickel 58.6	Cobalt 58.6
—	—	Copper 63.1	Zinc 64.9	—	Gallium 69.8	—	—	—	—	Arsenic 74.9	—	Selenium 79	—	Bromine 79.75	—	—	—	—
—	Rubidium 85.2	—	—	Strontium 87.2	—	Yttrium 89.6	—	—	Zirconium 90	—	Columbium 94	—	Molybdenum 95.6	—	Ruthenium 103.5	Rhodium 104.1	Palladium 106.2	—
—	—	Silver 107.66	Cadmium 111.6	—	Indium 113.4	—	—	—	Tin 117.8	Antimony 120	—	Tellurium 128?	—	Iodine 126.53	—	—	—	—
—	Cæsium 133	—	—	Barium 136.8	—	Lanthanum 139	Cerium 141.2	Didymium 147	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	Erbium 169	—	—	Tantalum 182	—	Tungsten 184	—	Osmium 198.6?	Iridium 192.7	Gold 196.2	Platinum 196.7
—	—	Mercury 199.8	—	—	Thallium 203.6	—	—	—	Lead 206.4	Bismuth 210	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	Thorium 231.5	—	—	—	Uranium 240	—	—	—	—	—

relations of the elementary substances; that is, not until he has mastered to some considerable degree the subject matter of chemistry. A few general considerations, however, may be of value in enabling him to form an estimate of the importance of the system here presented. The system involves two fundamental ideas, each of which has undoubtedly a large basis of truth. First, we have the idea of periodicity, or the recurrence of elementary atoms having similar relations at definite intervals as the atomic weight increases; and this feature of the classification is presented by the horizontal lines of our table. Secondly, in the vertical lines of the table we have exhibited several series of allied elements, in each of which the relations of the members vary according to some regular order. The idea of classification by series involves the grouping together, not simply of similar substances, but of substances which, while possessing in common certain general relations, differ in other respects, so that, although neighboring members of such a series may have a close resemblance, the distant members may have nothing in common except the one relationship which unites them all.

The idea of classification by series was first developed in the study of organic chemistry, where the principle is much more conspicuous than among inorganic compounds. Thus, as has been shown (§ 41), we are acquainted with a large number of acids resembling acetic acid, which form a series beginning with formic acid and ending with melissic acid. Each member of this series differs in composition from the preceding member by CH_2 or by some multiple of this symbol; and the properties of the compounds vary regularly between the extreme limits, according to well-established laws. Moreover, many other similar, although more limited, series of compounds are known, and the principle realized in these organic series seems to be the true idea of all chemical classification. But in attempting to apply it to the chemical elements, we find only two or three groups of atoms where the series is of sufficient extent to make the relations of the members evident. In most cases it would seem as if we only knew one or two members of a series, and this apparent

ignorance not only throws doubt on the general application of our principle, but also renders uncertain the details of our scheme, even assuming that the principle of the classification is correct. Hence, also, great differences of opinion may be reasonably entertained in regard to the position which the different atoms ought to occupy in such a scheme.

Another very important cause of uncertainty in any scheme of classifying the elements arises from the complex relationships which many of them manifest. Thus iron is in some of its relations closely associated with manganese and aluminum, while in others it is as closely allied to magnesium and zinc, and in still others it resembles — although much less closely — the elements with which it is associated in the table on page 267. Many other elements resemble iron in having a similar manifold character, and different authors may reasonably assign to such elements different places in their systems of classification, according as they view them from one or the other aspect. Hence arises a degree of uncertainty which affects our whole system, and which cannot be avoided in the present state of the science.

Indeed, no classification in parallel series can satisfy the complex relations of the elements, for these relations cannot be represented by any system of lines on a plane. The attempts which have been made only force upon our attention the fragmentary character of our knowledge, and the remarks already made in regard to the general scheme of chemical classification apply with equal force to the system of classifying the elements which has been described. It is quite evident that the qualities of the chemical elements are functions of several variables, of which one only is the atomic weight, and until we have a greater knowledge of the subject we cannot expect to discover the complex relationship which such a condition involves. Still, imperfect as it is, the scheme presented in the table furnishes a commanding, although partial, view of a complex subject, and may greatly aid the student in directing his study. The power of such a working theory to predict the order of undiscovered phenomena is a good criterion of its validity, and this system of classification predicted the relations and properties of the new

element gallium before it was isolated. Nevertheless, the system so frequently separates elements which, on account of their intimate relations, ought to be studied in connection, and brings together others which are allied only in their less prominent characteristics, that, in an elementary text-book, it cannot be strictly followed to advantage.* In Part II. of this work we have brought together, under the several subdivisions, those elements that resemble each other in the characteristics by which it seems to us most important for the student to associate them; beginning with those groups of elements which have the lowest degree of quantivalence, in order to present the simplest type of combination at the outset. As the prevailing quantivalence increases, the most characteristic and familiar compounds of the elements become more complex, and such an arrangement, therefore, has great advantages for a text-book, although of little value as a scientific classification.

120. **Relations of the Atomic Weights.** — In 1815 Dr. Prout, an English writer on chemistry, advanced the opinion that hydrogen, the lightest substance known, was the one primary condition of matter out of which all substances had been developed, and that the so-called elementary atoms were all aggregates of hydrogen atoms. Hence he concluded that the atomic weights of the substances regarded as elementary must all be exact multiples of the atomic weight of hydrogen, and this hypothesis has since been known as "Prout's law." But although the comparatively rude determinations of the atomic weights made before his time might be reconciled with this hypothesis, the subsequent progress of chemistry did not seem to confirm

* A Russian chemist, Mendelejeff, gave the form to the classification of the elements presented by the table on page 267, and we have reproduced the table as printed by Roscoe in his Treatise on Chemistry, without any essential alteration, although we consider that in many important respects it fails to present the true relations of the elements. We cannot alter it to conform to our own views of the facts without changing its essential character, and we question if it is possible, in the present state of chemistry, to substitute any other classification which would not be equally faulty. We therefore give the scheme as it has been usually printed, without change, only apprising the student that he must not expect that the facts as presented in Part II. will accord with it in all respects.

Prout's views. Most of the accurate experiments made for the purpose of fixing these constants gave incommensurable values, and this was especially true of a most noteworthy investigation undertaken by Professor Stas, of Brussels, with the view of testing Prout's hypothesis. His experiments, which were conducted with extreme care and with very large amounts of material, gave incommensurable values, and the results were thought at the time to show that the hypothesis in question was wholly illusory. Still it was remarkable that the values obtained by Stas differed from whole numbers only by a small fraction of a unit, and in the accurate determinations which have since been made by other chemists the same striking feature appears. In the table on page 267 we have copied intentionally the atomic weights as given by Roscoe (compare note above), while in the table on page 266 we have given the approximate values generally accepted (rather than the precise mean of the experimental work) in those cases where the difference is less than the probable error of the process employed.

In comparing these tables it must be borne in mind, in the first place, that, although there are some twenty of the atomic weights which may be regarded as accurate to a thousandth of their amount, and in a few cases possibly, to the ten-thousandth, yet in most cases the possible error in the determinations is as large as one per cent, while in several instances the atomic weight is not known within one tenth of the value given. Moreover, the errors we have chiefly to guard against in the determination of an atomic weight are not the "accidental errors," which can be eliminated by frequent repetitions of the same process, but "constant errors," arising from unknown impurities or from the imperfections of the process employed; and the closest agreement between repeated observations gives no sure indication of freedom from such errors as these.

In the second place, it must be remembered that the atomic weights of only a very few of the elements have been directly referred to the hydrogen unit, and that in most cases they are referred to this unit through the atomic weight of oxygen. Now one of the later determinations of Stas makes the atomic weight

of oxygen 15.96, instead of 16, the value accepted by Dumas as the most probable result after the discussion of a long series of careful and accordant determinations; and if we accept this value of Stas, and alter, as Roscoe has done, all the other weights given in the table on page 266 in the proportion of 16 : 15.96, it will be seen that the numbers of the two tables (pages 266 and 267) coincide except in the few cases where some point of theory is in question, and that both are based on essentially the same experimental evidence. On the other hand, if we assume $O = 16$ as the basis of the system, then $H = 1.0025$, according to Stas's determination; and it becomes equally evident that the difference between this and $H = 1.0000$ would be wholly imperceptible except in determinations on the scale of those of Stas, and even under such circumstances could only be distinguished, if at all, as a residual after the observations had been most carefully reduced. Yet, when the other atomic weights are reduced to the new basis by dividing by the common divisor 1.0025, the difference in the case of the larger atomic weights becomes very considerable, and gives the appearance of a much larger departure from Prout's law than really exists.

While, therefore, we do not question the great accuracy of Stas's work, we do not think it philosophical to change the basis of the system of atomic weights on the evidence of a single determination, which presents great experimental difficulties and is confessedly not of the highest order of accuracy; especially as we believe that the weight of evidence is in favor of the conclusion that, when the atomic weight of oxygen is sixteen, a very large number of the weights can be expressed by integers within the limits of probable error. In order to illustrate this point we give in the following supplementary table the twenty atomic weights which may be fairly considered as the only ones which have been determined within one thousandth of their amount, including the determinations of Stas, all on the basis that $O = 16.00$; and it will be noticed that, with the exception of the atomic weight of chlorine, the values differ in no case from a whole number by more than fifteen hundredths of an integer, and generally by much less.

ATOMIC WEIGHTS

MOST ACCURATELY DETERMINED.

Hydrogen	1.002	Chlorine	35.46
Lithium	7.01	Potassium	39.14
Carbon	12.00	Calcium	40.00
Nitrogen	14.04	Bromine	79.94
Oxygen	16.00	Silver	107.93
Aluminum	27.02	Antimony	120.00
Sodium	23.05	Iodine	126.85
Magnesium	24.00	Barium	137.14
Phosphorus	31.05	Thallium	204.11
Sulphur	32.07	Lead	206.91

If the atomic weights are in fact whole numbers, such slight differences from the true values as these in the observed results (excepting always the case of chlorine) are exactly what we should expect, seeing that no determinations of this kind can with certainty be freed from the influence of constant experimental errors. On the other hand, if the true weights are incommensurable and distributed by chance, the probability that the observed values would all lie so near to whole numbers as they do would be exceedingly small, and hence the total result, as far as it goes at present, may be said to confirm rather than invalidate Prout's hypothesis, and justifies the usual practice of selecting as the working atomic weight, not the precise mean of the experimental results of the most accredited investigators, but the nearest whole number, except in cases like chlorine, where the difference is evidently greater than the probable error. It is on this basis that the table on page 266, and also Table II. at the end of the volume, have been drawn up, and it is on this basis that the remarks which follow are made.

If the principle of classification by series is correct, and the elements actually belong to series like those of the compounds of organic chemistry, we should naturally expect that the atomic weights would conform to the same serial law; and it is a remarkable fact that the differences between the atomic weights

of the elements of the same group are in most cases very nearly multiples of 16. The value of this common difference varies between 15 and 17, and we must admit in some cases the simplest fractional multiples; but the mean value is very nearly 16, and the frequent occurrence of this difference is very striking. This numerical relation is not absolutely exact, but here, as in the periods of the planets, in the distribution of leaves on the stem of a plant, and in other similar natural phenomena, there is a marked tendency towards a certain numerical result, which is fully realized, however, only in comparatively few cases.

Other numerical relations which have been noticed between the atomic weights are probably only phases of the same law of distribution in series. Thus the atomic weight of sodium is very nearly the mean between that of lithium and potassium; and the atomic weights of chlorine, bromine, and iodine, of calcium, strontium, and barium, of oxygen, sulphur, and selenium, are similarly related. Again, there are several pairs of allied elements between whose atomic weights there is very nearly the same difference. Thus the difference between the atomic weights of indium and thallium is very nearly the same as that between the atomic weights of antimony and bismuth, and the difference between the atomic weights of columbium and tantalum the same as that between the atomic weights of molybdenum and tungsten. A careful study of the atomic weights will also reveal many other approximate relations of the same sort; but although the study of these relations is highly interesting, and may lead hereafter to valuable results, yet no great importance can be attached to them in the present state of the science.*

* See paper by the author on "The Numerical Relation between the Atomic Weights, with some Thoughts on the Classification of the Chemical Elements," in Memoirs of the American Academy, 1853.

PART II.

INTRODUCTION.

HAVING developed in Part I. the fundamental principles of chemical science, we shall now give, in Part II., a brief summary of the more important elements and compounds, exhibiting their constitution and relations by means of formulæ and reactions, and adding a number of questions and problems, which will serve to direct the attention of the student to the more important facts and principles, or to those which, being only implied in the context, might be otherwise overlooked, and which will also give him the means of testing the thoroughness and accuracy of his knowledge. The answers to the problems have been calculated with the four-place logarithms, which will be found at the end of the volume. Used in connection with the table of antilogarithms which accompanies them, the logarithms give results which are accurate to the fourth significant figure, and this degree of accuracy exceeds in almost every case that of the experimental data given in the problems. With certain exceptions referred to below, the answers to the questions are either stated or implied in the immediate context, or in the sections and formulæ to which reference is made. The references to sections are enclosed in parentheses, and those to formulæ in brackets. Direct questions on the facts stated in the summary are seldom given, and obviously would be superfluous; but the student should make himself thoroughly acquainted with the subject-matter of each section before he attempts to answer the questions or solve the problems which follow. In studying the book, however, he should aim to acquire a knowledge of the general principles and mutual relations which are exhibited, rather than to commit to memory the isolated facts. He must never forget that he is dealing, not with abstractions, but with real things and actual phenomena, and that chemical formulæ are merely expressions of definite facts ascertained

by experiment. Moreover, he must discriminate with the greatest care between the facts directly stated or expressed by the reactions and the inferences drawn from them, and he should be required to state clearly the successive steps in every process of inductive reasoning. As was stated in the Preface, this portion of the book is only intended as an auxiliary to lecture-room or laboratory instruction, and the closer the lessons can be connected with the experimental illustrations the better.

In classifying the chemical elements for the purposes of study we have had reference solely to their most conspicuous and familiar relations, — those relations by which the student will most readily associate them. Under each "Division" of Part II. we have brought together, as far as possible, those elements which obviously belong to the same family, or to the same chemical series, and when an element presents no such obvious relationship, have placed it in a division by itself. The larger of these divisions correspond in great measure to the vertical columns in the classification of Mendelejeff; but, for reasons already given, we have not followed that classification closely. In arranging the divisions we have followed the "prevailing quantivalence," beginning with the groups of elements having the smallest quantivalence, in order to present the simplest types of combination first, and afterward coming to those which are more complex. Here, again, we conform approximately to the horizontal lines in Mendelejeff's table, but not closely; because, if, according to the fundamental idea of his classification, we arrange the elements in the exact order of their atomic weights, a regular increase of atomicity on the horizontal lines can be made out only by bringing into prominence unusual aspects of many of the elements. In connection with each element we mention the more important compounds which it forms with the elements preceding it in our classification. At least this is the general rule; but so far as regards the compounds we do not follow this order invariably, departing from it whenever it may be necessary to illustrate the relations of the element we may be studying. Thus we describe with each element its chief oxygen and sulphur compounds from the first. No attempt has been made to embrace the whole field, but the aim has been to illustrate fully the principles of chemical philosophy, and to give a clear idea of that phase of the scheme of nature which has been revealed by the study of chemistry. As stated in the Preface, the "Questions and Problems" are an essential feature in the plan of the work, and

serve to supplement as well as to illustrate the text. The student will find that the knowledge which he gains inferentially while seeking the answers to the questions, or solving the problems, is peculiarly valuable, and the acquisition has something of the zest of new discovery. As he advances, he will meet with questions which he cannot fully answer without consulting more extended works, and which are intended to direct his study beyond the limits of this book. He may refer in such cases to Watts's Dictionary of Chemistry, Miller's Elements of Chemistry, Roscoe and Schorlemmer's Treatise on Chemistry, Wagner's Chemical Technology, Percy's Metallurgy, and Dana's System of Mineralogy, all of which are excellent works of reference.

PART II.

DIVISION I.

121. **HYDROGEN.** $H = 1$. — Univalent. The lightest atom, and the standard of quantivalence. Very widely diffused in nature. Forms one ninth of water, and is a constituent of almost all vegetable and animal substances, as well as of many minerals. The essential constituent of all acids and bases, from which it is readily displaced by other atoms.

122. **Hydrogen Gas.** *H-H.* — A gas which has been liquefied, and probably solidified, by extreme cold under great pressure. Standard of comparison for Sp. Gr. Seldom found in a free state in nature. Best prepared by the action of zinc or iron on dilute sulphuric acid.

$$\mathrm{Zn} + (H_2SO_4 + Aq) = (ZnSO_4 + Aq) + \mathrm{H\text{-}H}. \qquad [64]$$

Very combustible. Has the greatest calorific power of any substance. Aqueous vapor sole product of the burning.

$$2\,\mathrm{H\text{-}H} + \mathrm{O{=}O} = 2\,H_2O. \qquad [65]$$

123. **Hydric Oxide (Water).** H_2O. — The universally diffused liquid of the globe, and the chief constituent of organized beings. Standard of comparison for *Sp. Gr.* at 4°, point of maximum density. Below 0° a crystalline solid (hexagonal system, § 107). *Sp. Gr.* = 0.918. Under the ordinary pressure of the air it boils at 100°, but exists in the atmosphere in the state of vapor at all temperatures. For maximum tension of vapor at different temperatures, see Chem. Phys. §§ 284 and 312. Water is an almost universal solvent, and the medium of most chemical changes. Its molecular structure is regarded as the type of a very large class of chemical compounds. Its composition may be determined, — First, by electrolysis (§ 98 and [65] reversed). Second, by passing a mixture of steam and chlorine gas through a red-hot tube.

$$2\,H_2O + 2\,\mathrm{Cl\text{-}Cl} = 4\,\mathrm{HCl} + \mathrm{O{=}O}. \qquad [66]$$

Third, by exploding in an eudiometer-tube a mixture of oxygen and hydrogen gases [65]. Fourth, by passing hydrogen gas over heated cupric oxide.

$$CuO + H\text{-}H = Cu + H_2O. \qquad [67]$$

Water combines with anhydrides to form acids, as

$$SO_3 + H_2O = H_2{=}O{=}SO_2, \qquad [68]$$

or

$$P_2O_5 + 3\,H_2O = 2\,H_3{\equiv}O_3{\equiv}PO.$$

It combines with metallic oxides to form hydrates, bases, or alkalies, as

$$Na_2O + H_2O = 2\,Na\text{-}O\text{-}H \text{ or } CaO + H_2O = Ca{=}O_2{=}H_2. \qquad [69]$$

It combines with many salts as water of crystallization, as

$$Fe{=}SO_4 . 7\,H_2O \text{ Cryst. Ferrous Sulphate.}$$

124. **Hydroxyl.** *HO.* — A very important compound radical, which may be regarded as a factor (§ 23) in the molecules of many chemical compounds, and for this reason it is sometimes convenient to write its symbol *Ho*. The oxygen bases may be considered as compounds of hydroxyl with electro-positive atoms or radicals, and the oxygen acids as compounds of the same with electro-negative atoms or radicals. Thus we may write the symbols of the following compounds as shown below: —

Sodic Hydrate	$Na\text{-}O\text{-}H$	or	$Na\text{-}Ho$
Baric Hydrate	$Ba{=}O_2{=}H_2$	"	$Ba{=}Ho_2$
Ferric Hydrate	$[Fe_2]{\equiv}O_6{\equiv}H_6$	"	$[Fe_2]{\equiv}Ho_6$
Nitric Acid	$H\text{-}O\text{-}NO_2$	"	$Ho\text{-}NO_2$
Sulphuric Acid	$H_2{=}O_2{=}SO_2$	"	$Ho_2{=}SO_2$
Phosphoric Acid	$H_3{\equiv}O_3{\equiv}PO$	"	$Ho_3{\equiv}PO$

[70]

125. **Hydric Peroxide (Oxygenated Water).** H_2O_2 or $Ho\text{-}Ho$. — Best regarded as the "radical substance" (§§ 23 and 29) corresponding to hydroxyl. In its most concentrated form it is a colorless liquid of the consistency of syrup, and having a decided odor resembling chlorine. Soluble in water in all proportions. Prepared by action of carbonic dioxide on baric peroxide.

$$BaO_2 + (H_2CO_3 + Aq) = BaCO_3 + (H_2O_2 + Aq). \qquad [71]$$

Carbonic dioxide is passed through water in which BaO_2 is suspended, and the solution of H_2O_2 subsequently evaporated *in vacuo*. Decomposed by fine metallic powders, and also spontaneously at temperatures higher than 22°, into water and oxygen gas.

$$(2\,H_2O_2 + Aq) = (2\,H_2O + Aq) + \text{O=O}. \qquad [72]$$

It liberates iodine from its compounds.

$$2\,KI + (Ho\text{-}Ho + Aq) = \text{I-I} + (2\,K\text{-}Ho + Aq). \qquad [73]$$

It generally acts as an oxidizing agent.

$$PbS + (4\,H_2O_2 + Aq) = PbSO_4 + (4\,H_2O + Aq). \qquad [74]$$

It sometimes, however, acts as a reducing agent.

$$Ag_2O + (H_2O_2 + Aq) = Ag_2 + (H_2O + Aq) + \text{O=O}. \qquad [75]$$

QUESTIONS AND PROBLEMS.*

1. What distinction can be drawn between a chemical element and an elementary substance, it being understood that the word *element* is used in a restricted sense, as applying only to the ultimate atoms into which matter may be resolved? Illustrate the distinction by the case of hydrogen. (§§ 54, 19, and 23.)

2. What is the essential characteristic of an acid and of a base? (§§ 36 and 37.)

3. What is the ground for the belief that each molecule of hydrogen gas consists of two atoms? (§ 20.)

4. The litre and the crith, the molecular weight of hydrogen and its molecular volume, sustain what relation to each other? State the reason for the rule on page 68. (§§ 2 and 26.)

5. How many grammes of zinc, and how many of sulphuric acid, will yield one litre of hydrogen gas?

Ans. 2.92 grammes of zinc, and 4.39 grammes of sulphuric acid.

* It is assumed in all the problems of this book that the temperature is 0° C., and the pressure 76 c. m., unless otherwise stated. The following abbreviations will be used: c. m., centimetre; $\overline{\text{c. m.}^3}$, cubic centimetre; $\overline{\text{d. m.}^3}$, cubic decimetre; kilo., kilogrammes, etc. (See Table I.)

6. If 45 grammes of zinc are used in reaction [64], how many cubic centimetres of sulphuric acid must be used also, and how many grammes of zinc sulphate, and how many litres of hydrogen gas, will be formed in the process (*Sp. Gr.* of $H_2SO_4 = 1.843$)?

Ans. 36.7 $\overline{\text{c. m.}}^3$ of sulphuric acid, 111.3 grammes of zinc sulphate, and 15.4 litres of hydrogen.

7. What volume of water should be mixed with the sulphuric acid in the last problem, assuming that the reaction takes place at 20°, and that 100 parts of water at that temperature will dissolve 53 parts of zinc sulphate?

Ans. 209.9 $\overline{\text{c. m.}}^3$, or enough to dissolve all the zinc salt formed.

8. What weight of iron must be used to generate sufficient hydrogen to raise in the atmosphere by its buoyancy a total weight of 121 grammes (Sp. Gr. of air 14.5 nearly)?

Ans. 100 litres of hydrogen gas will be required, and this can be made from 250.9 grammes of iron.

9. Assuming that the principle of § 18 is correct, why does it follow from reaction [65] that the molecule of oxygen gas must contain at least two atoms?

10. What is the volume of 4.480 grammes of hydrogen at 273°.2 [10]?

Ans. 100 litres.

11. What is the volume of 4.480 grammes of hydrogen at 0° and under a pressure of 38 c. m. [4]? Ans. 100 litres.

12. A block of ice weighs 36.72 kilo. What is its volume [1]?

Ans. 40 $\overline{\text{d. c.}}^3$

13. An iceberg is floating in sea-water (*Sp. Gr.* = 1.028). What proportion of its bulk is submerged? Ans. 0.8932.

14. One kilogramme of steam at 100° will melt how many kilo. of ice?

Ans. The steam by condensing and cooling would give out 637 units of heat, which is adequate to melt $637 \div 79 = 8+$ kilogrammes of ice. (§§ 15 and 17.)

15. What is the weight of one litre of confined steam at the temperature of 144°? Tension of steam at 144° equals 4 atmospheres.

Ans. Weight of litre of steam at 0° and 76 c. m. would be theoretically 9 criths. Hence weight at 144° and 4×76 c. m. is, by [12], 2.358 criths, or 2.113 grammes.

16. What is the weight of one litre of superheated steam under normal pressure, and at 546°.4? Ans. 0.2688 gramme.

17. Water is forced into a glass globe containing dry air, at the temperature of 100° C. and under the normal pressure, as long as it continues to evaporate. What will be the tension of the moist air?

Ans. Water or any other liquid evaporates into a confined space until the vapor attains its maximum tension for the existing temperature, even when the space is filled with another gas; and the tension of the mixture of gas and vapor is equal to the sum of the tension which each would exert separately. (Chem. Phys. 312.) The maximum tension of aqueous vapor at 100° is 76 c. m., and hence the tension of the moist air in the globe must be 152 c. m.

18. A volume of hydrogen gas standing in a bell-glass over a pneumatic trough, and consequently saturated with moisture, measures 100 $\overline{\text{c. m.}}^3$. The temperature is 22°.3, and pressure on the gas 76 c. m. What would be the volume under the same conditions if the air were perfectly dry?

Ans. The maximum tension of aqueous vapor at given temperature is 2 c. m. Hence, if vapor were removed, the tension of the gas would become 74 c. m., provided the volume remained constant. But the exterior pressure being 76 c. m., the volume must accommodate itself to this condition, and hence by [4] would be reduced to 97.36 c. m.

19. What is the Sp. Gr. of aqueous vapor? What is meant by the term Sp. Gr. as applied to a vapor, and under what conditions is it assumed to be taken? (§§ 1 and 18). Ans. 9.

20. In Table III. the weight of one litre of aqueous vapor under the standard conditions of temperature and pressure is given as 9 criths. Why is this value a fiction? and why is an impossible value given in the table? (Chem. Phys. § 329.)

21. In the experiment indicated by reaction [66] the oxygen gas was collected in a bell-glass over water. It measured 1,101 $\overline{\text{c. m.}}^3$ at the temperature 22°.3 and under a pressure of 76 c. m. What was the volume of chlorine gas used, measured under the normal conditions? The tension of aqueous vapor at 22°.3 is 2 c. m. Ans. 2 litres.

22. How much copper will be *reduced* in the formation of 9 grammes of water, and what volume of hydrogen gas will be used in the reaction?

Ans. 31.7 grammes of copper, and 11.16 litres of hydrogen.

23. It has been found by exact experiments that for every 9 grammes of water formed by reaction [67] the cupric oxide lost in weight 8 grammes. What is the percentage composition of water?

Ans. 11.112 of hydrogen, and 88.888 of oxygen.

24. Given percentage composition of water and the Sp. Gr. of aqueous

vapor, and assuming that the molecule of water contains only one oxygen atom, how can you deduce the atomic weight of oxygen? (§ 24.)

25. Assuming that all the heat of combustion is utilized, how many litres of hydrogen must be burnt to convert into free steam one kilogramme of boiling water, and how does the volume of steam generated compare with the volume of gas burnt?

Ans. 176.8 litres of hydrogen gas, and 1,240 litres of steam, when reduced to standard conditions. (§§ 15, 18, and 66.)

26. Assuming that all the heat of combustion is retained in the aqueous vapor formed from the burnt hydrogen, how will the volume of the expanded vapor compare with that of the gas consumed?

Ans. By problem on page 162 it appears that the temperature of the vapor would be, under the conditions assumed, 6,853°. Hence by [11] the volume would be 26.08 times as great as that of the gas.

27. Assuming that the whole volume of gas resulting from the electrolysis of water is retained in the space previously occupied by the water, what would be its tension? Ans. 1,860 atmospheres.

28. What is the relation of an anhydride to an acid, or of a metallic oxide to a hydrate? (§§ 38 and 48.)

29. What objections may be raised to the method of writing the symbols of acids and bases used in [70]?

30. What is the distinction between a compound radical and a radical substance?

31. Why does reaction [73] sustain the view that hydric peroxide contains the radical hydroxyl? Do not reactions [72], [74], and [75] point to another view of its constitution?

32. Analyze reaction [75], and show that it is in harmony with the modern theory of the constitution of the oxygen molecule.

33. Can you explain reactions like [121] on any other theory than the one suggested in the context?

DIVISION II.

126. **FLUORINE.** $F = 19$. — Quantivalence usually one. A chief constituent of fluor-spar, CaF_2, and of cryolite, $Na_6Al_2F_{12}$. Found also, but in small quantities, in apatite, tourmaline, mica, and a few other minerals. Also in the bones of animals, especially in the teeth. The elementary substance F-F is probably a gas, but it has not with certainty been isolated.

127. **Hydrofluoric Acid.** HF. — The anhydrous acid is at 15° a colorless mobile liquid, extremely volatile, boiling at 19°.5, densely fuming in the air, and attracting greedily water from the atmosphere. It is exceedingly corrosive, and a highly dangerous substance. The dilute acid is obtained by distilling a mixture of powdered fluor-spar and sulphuric acid in a platinum or lead retort.

$$CaF_2 + (H_2SO_4 + Aq) = CaSO_4 + 2\,HF + Aq. \quad [76]$$

Cryolite may be used instead of fluor-spar. This acid is distinguished for its power of dissolving silica, with which it forms volatile products. Hence it is much used in chemical analysis for decomposing siliceous minerals, and in the arts for etching glass.

128. **CHLORINE.** $Cl = 35.5$. — Quantivalence usually one, but probably also of higher uneven orders. Very widely distributed in nature, chiefly in combination with sodium, forming common salt.

129. **Chlorine Gas.** Cl-Cl. — Yellowish-green gas, which may be liquefied by pressure, but has never been frozen. Soluble in water, with which it forms at 0° a crystalline hydrate. Highly corrosive, and enters into direct union with most of the elementary substances. Discharges vegetable colors and destroys noxious effluvia, and hence much used in the arts as a bleaching and disinfecting agent. Prepared by gently heating in a glass flask a mixture of hydrochloric acid and manganic dioxide.

$$MnO_2 + (4\,HCl + Aq) = (MnCl_2 + 2\,H_2O + Aq) + Cl\text{-}Cl. \quad [77]$$

Chlorine gas is a very important chemical reagent. It not only converts many simple chlorides into perchlorides, but, with the intervention of water or of some other oxygen compound, it also acts as an

oxidizing agent, and to this effect its bleaching power is probably in great measure owing.

$$(SnCl_2 + Cl_2 + Aq) = (SnCl_4 + Aq). \quad [78]$$

$$3\,Ni(HO)_2 + (Cl\text{-}Cl + Aq) = [Ni_2](HO)_6 + (NiCl_2 + Aq). \quad [79]$$

When the aqueous solution is exposed to direct sunlight, a reaction like [66] results, and oxygen gas is set free. Chlorine has also a remarkable power of replacing hydrogen in many of its compounds. (§ 30.)

130. **Hydrochloric Acid.** *H-Cl.* — A colorless gas which may be liquefied by cold and pressure, but has not been frozen. Exceedingly soluble in water, which at 4° absorbs its own weight, or about 480 times its volume, of the gas. This solution is very much used in the laboratory as a reagent, and an impure solution called muriatic acid is manufactured on a large scale for the uses of the arts. From the *Sp. Gr.* of the liquid acid we can determine very closely the quantity of gas held in solution, by means of tables in which the results of careful experimental determinations have been tabulated. The following extracts from a table by Dr. Ure give all the data required for calculating the problems in this book.

Sp. Gr. 15° C.	Per Cent *HCl.*	*Sp. Gr.* 15° C.	Per Cent *HCl.*	*Sp. Gr.* 15° C.	Per Cent *HCl.*	*Sp. Gr.* 15° C.	Per Cent *HCl.*
1.2000	40.777	1.1410	28.544	1.0899	18.349	1.0397	8.155
1.1893	38.330	1.1308	26.505	1.0798	16.310	1.0298	6.116
1.1802	36.292	1.1206	24.466	1.0697	14.271	1.0200	4.078
1.1701	34.252	1.1102	22.426	1.0597	12.233	1.0100	2.039
1.1599	32.213	1.1000	20.388	1.0497	10.194	1.0060	1.124

Pure hydrochloric acid is prepared in the laboratory by heating common salt with about twice its weight of sulphuric acid in a glass flask, and conducting the gas formed into large glass vessels containing water.

$$NaCl + (H_2SO_4 + Aq) = (H,NaSO_4 + Aq) + HCl. \quad [80]$$

In the arts, however, only one half as much sulphuric acid is used, but then the materials must be heated to a much higher temperature, and large iron retorts are employed.

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl. \quad [81]$$

Hydrochloric acid may also be obtained by directly uniting hydrogen and chlorine gas.

$$\mathbf{H\text{-}H} + \mathbf{Cl\text{-}Cl} = 2\,\mathbf{HCl}. \qquad [82]$$

By electrolyzing the aqueous solution, the last reaction is reversed and the acid is decomposed. It may also be readily decomposed by metallic sodium.

$$2\,\mathbf{HCl} + \mathbf{Na\text{-}Na} = 2\,\mathbf{NaCl} + \mathbf{H\text{-}H}. \qquad [83]$$

Liquid hydrochloric acid dissolves most of the metals and the metallic oxides, and its uses in practical chemistry are illustrated by the following reactions. See also [77].

$$\mathbf{Sn} + (2\,HCl + Aq) = (Sn\,Cl_2 + Aq) + \mathbf{H\text{-}H}. \qquad [84]$$

$$\mathbf{ZnO} + (2\,HCl + Aq) = (Zn\,Cl_2 + H_2O + Aq). \qquad [85]$$

$$\mathbf{[Al_2]O_3} + (6\,HCl + Aq) = ([Al_2]Cl_6 + 3\,H_2O + Aq). \qquad [86]$$

131. **Compounds of Chlorine and Oxygen.** — All of them unstable, and most of them explosive. In regard to their molecular constitution different views are entertained, and the following symbols, which represent chlorine as a multivalent atom, must not be regarded as established.

Hypochlorous Acid	$H\text{-}O\text{-}\overset{\text{I}}{Cl}$	Hypochlorous Oxide	Cl_2O
Chlorous Acid	$H\text{-}O\text{-}\overset{\text{III}}{Cl}O$	Chlorous Oxide	Cl_2O_3
Chloric Acid	$H\text{-}O\text{-}\overset{\text{V}}{Cl}O_2$	Chloric Dioxide	ClO_2
Perchloric Acid	$H\text{-}O\text{-}\overset{\text{VII}}{Cl}O_3$		

The following scheme will show how the possible acids and oxides of a multivalent radical may be classified.

	Hypochlorous Acids.	Chlorous Acids.	Chloric Acids.	Perchloric Acids.
Ortho-acid	$H\text{-}O\text{-}\overset{\text{I}}{Cl}$	$H_3{\equiv}O_3{\equiv}\overset{\text{III}}{Cl}$	$H_5{\equiv}O_5{\equiv}\overset{\text{V}}{Cl}$	$H_7{}^{\text{VII}}O_7{}^{\text{VII}}Cl$
First Anhydride	Cl_2O	$H\text{-}O\text{-}ClO$	$H_3{\equiv}O_3{\equiv}ClO$	$H_5{\equiv}O_5{\equiv}ClO$
Second "		Cl_2O_3	$H\text{-}O\text{-}ClO_2$	$H_3{\equiv}O_3{\equiv}ClO_2$
Third "			Cl_2O_5	$H\text{-}O\text{-}ClO_3$
Fourth "				Cl_2O_7

When the number of hydroxyl groups equals the quantivalence of the elementary radical, we distinguish the acid by the prefix *ortho*, as ortho-chloric acid, and for the successive anhydrides we may use the prefixes *meta*, *dimeta*, etc. These anhydrides are formed from the ortho-molecules by withdrawing successive molecules of water; or, as in the last step in each of the above series, by withdrawing a molecule of water from a double molecule of the compound. By comparing the scheme of possible compounds with the list of actual compounds above, it will be seen that only one ortho-acid of chlorine is known. The other known acids are all anhydrides, and we have no reason to hope that the corresponding ortho-acid will ever be obtained. But it is often possible to form the salts of an acid when the acid itself cannot be isolated. It will be noticed that the oxide ClO_2, or possibly Cl_2O_4, is not one of the above series of anhydrides. It is, however, one of the best defined oxides of chlorine, and although its molecular structure has not yet been determined, it may help the student to understand the scheme of classification, if he seeks to inquire what are the possible relations of this compound to the scheme. We present the scheme in this connection, not on account of the importance of the compounds here classified, but because it is important that the student should become early acquainted with a system which serves to co-ordinate a large number of facts. It is here presented in its simplest phase, and more complex relations of the same scheme will be explained under Boron and Silicon.

132. **Potassic Chlorate.** — The most important salt of any of the chlorine oxygen acids. Obtained by passing a stream of chlorine gas through a warm solution of caustic potash.

$$(6\,K\text{-}O\text{-}H + Aq) + 3\,Cl\text{-}Cl = (KClO_3 + 5\,KCl + 3\,H_2O + Aq). \qquad [87]$$

Potassic chlorate, being much the less soluble, is readily freed from the potassic chloride by two or three crystallizations. It is decomposed by heat alone into potassic chloride and oxygen gas.

$$2\,KClO_3 = 2\,KCl + 3\,\textcircled{O}\text{-}\textcircled{O}. \qquad [88]$$

Much used for making oxygen gas, and also in fireworks and in the preparation of detonating powder.

133. **BROMINE.** $Br = 80$. — Quantivalence like chlorine. Associated with chlorine in minute quantities in saline waters and certain

silver ores. The elementary substance (*Br-Br*) is a very volatile deep-red liquid. *Sp. Gr.* = 3.187. Boils at 63°. Freezes at 7°.3. Prepared from the bittern of certain salt springs, by treating with chlorine and dissolving out the liberated bromine with ether.

134. **Hydrobromic Acid.** *HBr.* — A colorless gas liquefying at −73° and freezing at −87°. It fumes in the air and is exceedingly soluble in water. When pure the aqueous solution is colorless and permanent in the atmosphere, but less stable than hydrochloric acid. Reactions similar to those of hydrochloric acid. An aqueous acid containing 47.75 per cent of *HBr* boils at 128°, and distils unchanged under the normal atmospheric pressure. This acid is best made by dissolving potassic bromide in its own weight of hot water, and adding to the hot solution seven parts of concentrated sulphuric acid previously mixed with one part of water and cooled. On standing, hydropotassic sulphate crystallizes out, and the acid solution is then distilled. Hydrobromic acid gas may be prepared by dropping liquid bromine very cautiously on amorphous phosphorus under water.

$$P + 4\,H_2O + 5\,Br = H_3PO_4 + 5\,HBr. \qquad [89]$$

135. **Bromine and Oxygen.** — No oxides of bromine have been obtained, but three acids corresponding to those of chlorine have been described: —

Hypobromous Acid	$HBrO$
Bromic Acid	$HBrO_3$
Perbromic Acid	$HBrO_4$

The last has not been isolated, but its salts are known.

136. **IODINE.** I = 16.8 — Quantivalence like chlorine. Associated with chlorine in still smaller quantities than bromine. The elementary substance is obtained from the ashes of certain seaweeds, and from the saltpetre of Atacama. Crystalline solid; *Sp. Gr.* = 4.95. Melts at 107°. Boils at 175°, forming a dense violet vapor. Very slightly soluble in water, but is readily dissolved by alcohol, ether, and carbonic sulphide. Imparts to starch paste a deep blue color.

137. **Hydriodic Acid.** *HI.* — A colorless gas which may be liquefied and frozen. Prepared by the action of iodine on amorphous phosphorus and water; reaction like [89]. Easily decomposed by heat into iodine and hydrogen. Fumes in the air, and is very soluble in water. Aqueous solution can be prepared by passing H_2S into water in which iodine is suspended.

$$I_2 + (H_2S + Aq) = S + (2\,HI + Aq). \qquad [90]$$

The aqueous acid is rapidly decomposed by the oxygen of the air, which unites with its hydrogen, when the liberated iodine dissolving in the liquid imparts to it a deep-red color.

138. **Iodine and Oxygen.** — Iodic acid, HIO_3, may be readily prepared by boiling iodine with concentrated nitric acid.

$$3\,I_2 + 10\,HNO_3 = 6\,HIO_3 + 2\,H_2O + 10\,NO. \qquad [91]$$

On concentrating the resulting solution we obtain a white crystalline solid, which at 200° loses water and forms a white powder which is the only known oxide of iodine, I_2O_5, and readily recombines with water, dissolving in the liquid with evolution of heat. At 300° the oxide decomposes into iodine and oxygen. Combustible bodies deflagrate when heated with iodic acid or with iodic oxide, and when in solution the acid is reduced by SO_2, by H_2S, and also by HI. We should expect to find iodic acid monobasic, yet it forms not only acid, but also diacid salts. In order to reconcile these facts with the univalence of iodine, it has been usual to regard the acid salts as molecular compounds, and the symbols of the potassium salts have been written thus :

$$KIO_3 \qquad KIO_3 . HIO_3 \qquad KIO_3 . 2\,HIO_3$$

but their constitution can be more reasonably represented on the theory that iodine is multivalent, according to the scheme of § 131.

Sodium iodate occurs in minute quantities in Chili saltpetre, and is one of the sources of iodine.

Periodic acid, $HIO_4 + 2\,H_2O$, formed by the action of iodine on aqueous perchloric acid, is a colorless deliquescent solid, which is completely decomposed at 140° into iodic oxide, water, and oxygen. The periodates have, as a rule, a very complicated structure, which is not fully understood, and can with difficulty be explained on the supposition that iodine is always univalent.

139. **Iodine and Chlorine.** — The two compounds ICl and ICl_3 have both been obtained as colorless crystalline solids, but they are exceedingly unstable. A compound of iodine and bromine, and perhaps also one of bromine and chlorine, have been formed, but they are so unstable that their constitution has not been determined.

The three elements chlorine, bromine, and iodine form a well-defined natural group, and a careful comparison will show that the

properties both of the elementary substances and of their compounds conform closely to the law of progression which marks a chemical series. These elements are all highly electro-negative bodies, but as we descend in the series we find that this character becomes less marked, and hence their chemical energy, as manifested by the strength of their affinity for elements of the opposite class, such as hydrogen and the electro-positive metals, diminishes as the atomic weight increases; and this law, as will appear, obtains with few exceptions in all the chemical series. Moreover, it will also be found, as might indeed be anticipated, that elements so closely related as these are almost invariably found associated in nature.

140. **Characteristic Reactions.** — The soluble chlorides, bromides, and iodides all give, with a solution of argentic nitrate, precipitates insoluble in water and dilute acids. The iodide of silver may be distinguished from both the chloride and the bromide of the same metal by its yellow color and insolubility in aqua ammonia, in which the last two dissolve, and the chloride much more readily than the bromide. Bromine and iodine may both be expelled from their salts by chlorine, when the first may be recognized by the red color which it imparts to ether or chloroform, and the last by the exceedingly characteristic blue color which it gives to starch paste. Fluorine is easily discovered because its compounds, when heated in a glass tube with potassic bisulphate, yield hydrofluoric acid, which etches the glass. This element, although closely allied to the other three, differs so greatly in some of its chemical relations that it is doubtful whether it belongs to the same chemical series.

QUESTIONS AND PROBLEMS.

1. It appears that 10 grammes of pure fluor-spar yield 17.436 grammes of calcic sulphate. [76.] Assuming that the atomic weight of calcium is 40, that of SO_4 to be 96, and also that the symbol of fluor-spar is CaF_2, what is the atomic weight of fluorine? Ans. 19.

2. How much fluor-spar and how much sulphuric acid must be used to generate sufficient hydrofluoric acid to neutralize 53 grammes of sodic carbonate? Ans. 39 grammes of fluor-spar, and 49 of sulphuric acid.

3. How much liquid hydrochloric acid, *Sp. Gr.* 1.1893, and how much MnO_2, will yield one litre of chlorine gas?

Ans. 3.897 grammes of MnO_2, and 17.06 grammes of hydrochloric acid.

4. In [77] $K_2Cr_2O_7$ may often be conveniently used in place of MnO_2. Write the reaction, knowing that $(Cr_2Cl_6 + Aq)$ is one of the products.

5. Fifty-nine grammes of metallic tin were dissolved in hydrochloric acid [84], and into this solution chlorine gas was passed until all the tin was converted into perchloride. How many litres of hydrogen gas were evolved in the first process, and how many of chlorine gas absorbed in the second?

Ans. 11.16 litres of each.

6. Analyze reaction [79], and show in what way the chlorine gas acts as an oxidizing agent.

7. Write the reaction which takes place when an aqueous solution of chlorine is exposed to the sun's direct rays. How far does this explain [79]?

8. Five grammes of liquid hydrochloric acid are mixed with a solution of argentic nitrate, the last being in excess. The precipitated argentic chloride was collected, washed, dried, and weighed. The weight was 3.206 grammes. Required the per cent of HCl in the solution. Ans. 16.31.

9. One volume of common muriatic acid, *Sp. Gr.* 1.2, contains how many volumes of HCl gas?

Ans. 1 $\overline{\text{c. m.}}^3$, or 1.200 grammes, contains 0.489 gramme of HCl, or 315.8 $\overline{\text{c. m.}}^3$ measured at 15°. [9.]

10. In order to make one litre of common muriatic acid of *Sp. Gr.* 1.16, how much salt and how much sulphuric acid must be used, and how much water must be placed in the condenser? [81.]

Ans. 598.9 grammes of salt, 1003 grammes of sulphuric acid, and 786.3 grammes of water.

11. On what does the economy of the process [81] over [80] depend?

12. The process [81] undoubtedly takes place in two stages. One half of the HCl is given off at low temperature, but it is necessary to heat the retort to a red heat to drive off the last portions. What are the two stages? Write the reaction of the second stage.

13. The reaction [82] is said to prove that both hydrogen and chlorine gas have molecules consisting of two atoms. On what postulates does the proof rest? (§§ 18 and 19.)

14. One litre of hydrochloric acid gas will yield by [83] how many litres of hydrogen gas? Ans. ½ of a litre.

15. Point out the differences between the reactions [84, 85, 86, and 77], and the relations on which the differences depend.

16. Show that the compounds of chlorine and oxygen may be regarded as compounds of chlorine and hydroxyl, less a certain number of molecules of water. What quantivalence would it then be necessary to assign to chlorine?

Ans. For one case, $(HO)_7{}^{VII}\overset{VII}{Cl} - 3H_2O = (HO)\text{-}\overset{VII}{Cl}O,O,O.$

17. It has been found by very careful experiments that 100 parts of potassic chlorate yield by [88] 60.85 parts of potassic chloride; and, further, that 100 parts of potassic chloride give by precipitation 192.4 parts of argentic chloride. Assuming that the symbols of these compounds are those given above, what must be the atomic weights of chlorine, potassium, and silver? It is also assumed, as found by previous experiments, that the atomic weight of oxygen is 16, and that 100 parts of silver combine with 32.87 of chlorine. Ans. $Cl = 35.5$, $K = 39.1$, $Ag = 108$.

18. The chlorine gas evolved from 1.740 grammes of MnO_2 is passed into a solution of potassic iodide. How much iodine will be thus set free?

Ans. 5.081 grammes.

19. When chlorine is passed into a cold dilute solution of KOH, the salt $KOCl$ is formed; but if the solution is hot or concentrated, $KClO_3$ is formed, and the other products in each case are KCl and H_2O. Write the reactions.

20. When potassic chlorate is cautiously heated to a few degrees above its melting point, and maintained at that temperature, it is found that, after one third of its oxygen has been driven off, the melted salt becomes again nearly solid, and must be heated to a higher temperature to expel the remainder of the oxygen. When the change is arrested at the end of the first stage, the white residue is a mixture of potassic perchlorate and potassic chloride. Write the reaction.

21. When bromine water is shaken up with HgO, a solution of hypobromous acid is formed. Write the reaction.

22. When bromine is dissolved in a solution of potassic or sodic hydrate, a bromate of these alkaline bases is formed. Write the reaction.

23. Bromate of silver is precipitated on the addition of argentic nitrate to a solution of an alkaline bromate, and a solution of bromic acid may be obtained by treating the silver salt suspended in water with bromine. Write the reactions.

24. A solution of bromic acid is reduced by SO_2, by H_2S, and by HBr. In addition to free bromine the products are either sulphuric acid, sulphur, or water. Write the reactions.

25. Iodic acid may be formed by the action of chlorine gas on iodine suspended in water. The chlorine decomposes the water by uniting with its hydrogen. Write the reaction.

26. Assuming that iodine is multivalent, can you write the symbols of the acid potassic iodates in a more probable form? Make a scheme of the possible acids and oxides of iodine.

27. In testing for iodine with chlorine water and starch, why is it important to avoid an excess of chlorine? (§ 139.)

28. It appears from recent experiments that, while below 700° the (Sp. Gr.) of iodine vapor is 8.73, above 1,400° it is only about one half of this amount, the density decreasing as the temperature rises, and reaching a minimum at the temperature stated. What conclusion do you draw from these facts in regard to the molecule of iodine in these two conditions? Do they have any bearing on the question discussed in § 54? If at high temperatures atoms can be isolated and act as molecules, may they not act in a similar way at low temperatures? We know that magnetic polarity is destroyed by heat. May not that mode of chemical polarity which we conventionally represent by atomic bonds be similarly affected (§ 90)? Do not such considerations bear on the question of variable quantivalence? Review in this connection the molecular structure of the oxides of nitrogen.

DIVISION III.

141. **SODIUM.** $Na = 23$. — Univalent. Combined with chlorine it forms common salt, a substance which is very widely distributed throughout nature. It also enters into the composition of a few other minerals as an essential constituent, and several of its salts find important applications both in the arts and in common life.

142. **Metallic Sodium.** *Na-Na.* — Soft, white metal, with brilliant lustre, but rapidly tarnishing in the air. *Sp. Gr.* = 0.97. Fuses at 90°, and boils at a red heat. Sp. Gr. = 22.8. When heated in the air, it burns with intensely yellow flame, the chief product being Na_2O_2. Decomposes water at the lowest temperatures. Prepared by distilling a mixture of sodic carbonate and charcoal in an iron retort.

$$Na_2CO_3 + 2\,C = Na\text{-}Na + 3\,CO. \qquad [92]$$

Used in the extraction of aluminum, and in the chemist's laboratory as a powerful reducing agent.

143. **Sodic Chloride (Common Salt).** *NaCl.* — White crystalline salt (isometric, Fig. 27). *Sp. Gr.* = 2.078. Melts at red heat. Volatilizes at white heat. Soluble in about three times its weight of water. Obtained from salt beds and by the evaporation of saline waters. An essential article of food. The source of almost all the sodium salts. Used for preserving meat.

144. **Sodic Carbonate.** Na_2CO_3. — The crystallized salt contains in addition $10\,H_2O$ (*Sal Soda*), but effloresces in dry air. White soluble salt, having an alkaline reaction. Formerly prepared by the lixiviation of the ashes of certain marine plants called barilla. In the United States it is obtained to a limited extent from cryolite (§ 126); but the great mass of the soda of commerce is chiefly made from common salt by Leblanc's process. This consists, — First, in treating common salt with sulphuric acid, which in two stages converts sodic chloride into sodic sulphate (Prob. 10, page 290).

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl. \qquad [93]$$

Secondly, in melting on the hearth of a reverberatory furnace the sodic sulphate with chalk and fine coal, a process in which the two following reactions take place simultaneously: —

$$5\,Na_2SO_4 + 20\,C = 5\,Na_2S + 20\,CO. \quad [94]$$

$$5\,Na_2S + 7\,CaCO_3 = 5\,Na_2CO_3 + 5\,CaS,\ 2\,CaO + 2\,CO_2. \quad [95]$$

Thirdly, by lixiviating the non-volatile product of the last reaction (called black-ball) with water, which dissolves only the sodic carbonate. Used in washing, in the manufacture of glass and soap, and in the preparation of other sodium salts. Also an important reagent in the laboratory. Precipitates most of the metals from solution of their salts, generally as carbonates.

$$(CaCl_2 + Na_2CO_3 + Aq) = CaCO_3 + (2\,NaCl + Aq). \quad [96]$$

When fused in large excess with insoluble silicates or sulphates, it decomposes them. Sodic silicate or sulphate is formed, which is soluble in water, and metallic carbonates, soluble in acids.

$$BaSO_4 + x\,Na_2CO_3 = BaCO_3 + Na_2SO_4 + (x - 1)\,Na_2CO_3. \quad [97]$$

145. **Acid Sodic Carbonate (Bicarbonate of Soda).** $H,Na\text{-}CO_3$. — The crystallized neutral carbonate, when exposed to an atmosphere of carbonic anhydride, absorbs the gas, and is converted into this product (a white powder).

$$Na_2CO_3 . 10\,H_2O + CO_2 = 2\,H,Na\text{-}CO_3 + 9\,H_2O. \quad [98]$$

Used, under the name of saleratus, for raising bread, and in the preparation of various effervescing powders.

$$(H,Na\text{-}CO_3 + \underset{\text{Cream of Tartar.}}{H,K\text{-}C_4H_4O_6} + Aq) =$$

$$\underset{\text{Rochelle Salts.}}{(Na,K\text{-}C_4H_4O_6} + H_2O + Aq) + CO_2. \quad [99]$$

146. **Sodic Hydrate (Caustic Soda).** $Na\text{-}O\text{-}H$. — Amorphous white solid, having very strong attraction for water, in which it dissolves in all proportions, evolving considerable heat. Solution powerfully alkaline and strongly caustic. Prepared by adding milk of lime to a solution of sodic carbonate.

$$(Na_2\text{-}CO_3 + Ca\text{-}(HO)_2 + Aq) = Ca\text{-}CO_3 + (2\,Na\text{-}HO + Aq). \quad [100]$$

To obtain the solid, the solution must be decanted from the insoluble chalk ($CaCO_3$) and evaporated to dryness. The solution itself is a very valuable reagent in the laboratory, and a crude solution (lye) is used in the arts for making soap. Caustic soda will completely sa-

tralize the strongest acids. On evaporating the neutral solution, we obtain the sodic salt of the acid used.

$$(Na\text{-}O\text{-}H + HO\text{-}NO_2 + Aq) = Na\text{-}O\text{-}NO_2 + H_2O + Aq). \quad [101]$$

$$(2\,Na\text{-}O\text{-}H + \underset{\text{Oxalic Acid.}}{(HO)_2{=}C_2O_2} + Aq) = ((Na\,O)_2{=}C_2O_2 + 2\,H_2O + Aq). \quad [102]$$

Sodic salts of weak acids have an alkaline reaction.

147. **Oxides of Sodium.** — Sodic Oxide, $Na_2{=}O$. Sodic Peroxide, $Na_2{=}(O\text{-}O)$.

148. **Sodic Nitrate (Saltpetre, Cubic Nitre).** $Na\text{-}No_3$. — A natural product found incrusting the soil in the desert of Atacama. Crystallizes in rhombohedrons resembling cubes. Much used for making nitric acid.

149. **POTASSIUM.** $K = 39.1$. — Univalent. An important constituent of felspar and mica, two very widely distributed silicious minerals. A constituent also of all fertile soils which are formed in part by the disintegration of rocks containing these minerals. By the action of atmospheric agents on the soil, soluble potassium salts are formed, which are absorbed by the growing plants whose ashes are the chief source of the potassium salts of commerce. But these salts are now also obtained from the salt beds of Stassfurt in Germany.

150. **Metallic Potassium.** $K\text{-}K$. — Resembles sodium, but has a bluish tinge of color; *Sp. Gr.* = 0.865. Brittle at 0°. Soft at 15°. Melts at 55°. Sublimes in green vapors at a low red heat. Burns when heated in the air, and takes fire spontaneously on water. Prepared by distilling in an iron retort the intimate mixture of potassic carbonate and charcoal obtained by charring crude tartar. Reaction same as [92], substituting K for Na. More powerful reducing agent than sodium; hence obtained with greater difficulty. More expensive, and less used on that account.

151. **Potassic Carbonate.** K_2CO_3. — White deliquescent salt, with strong alkaline reaction. The crude salt (*Potashes* of commerce) is obtained by lixiviating wood-ashes and evaporating the lixivium. Purified by dissolving in a small quantity of boiling water, and crystallizing out the impurities. Largely consumed in the arts for manufacturing glass and soap, and for preparing other compounds of potassium.

152. **Acid Potassic Carbonate (Bicarbonate of Potash).** $H,K{=}CO_3$. — White crystalline salt, prepared by passing CO_2 through

a strong solution of the neutral carbonate. Reaction like [98], substituting *K* for *Na*.

153. **Potassic Hydrate (Caustic Potash).** $H,K\text{-}O$. — White amorphous solid, prepared like caustic soda [100], which it closely resembles, but is more deliquescent and more strongly alkaline. Forms with fats "soft soaps," while soda forms "hard soaps." Like caustic soda, an important reagent in the laboratory. Precipitates from solutions of their salts most of the metals, generally as hydrates, but sometimes as oxides. In some cases the precipitate is soluble in an excess of the reagent.

$$(Ca\text{=}SO_4 + 2\,K\text{-}(HO) + Aq) = \mathbf{Ca\text{=}(HO)_2} + (K_2\text{=}SO_4 + Aq). \quad [103]$$

$$(2\,Ag\text{-}NO_3 + 2\,K\text{-}(HO) + Aq) = \mathbf{Ag_2O} + (H_2O + 2\,K\text{-}NO_3 + Aq). \quad [104]$$

$$([Al_2]Cl_6 + 6K\text{-}(HO) + Aq) = \mathbf{[Al_2]\equiv(HO)_6} + (6\,KCl + Aq). \quad [105]$$

$$\mathbf{[Al_2]\equiv(HO)_6} + (6\,K\text{-}HO + Aq) = \underset{\text{Potassic Aluminate.}}{(K_6\equiv O_6\equiv[Al_2]} + 6\,H_2O + Aq). \quad [106]$$

154. **Oxides of Potassium.** — Potassic Oxide, $K_2\text{=}O$. Potassic Dioxide, $K_2\text{=}(O\text{-}O)$. Potassic Tetroxide, $K_2\text{=}(O\text{-}O\text{-}O\text{-}O)$.

155. **Potassic Chloride (Sylvine).** KCl. — Isomorphous with $NaCl$. Found associated with Carnallite ($KCl\,.\,MgCl_2\,.\,6\,H_2O$) in the mines of Stassfurt.

156. **Potassic Nitrate (Nitre).** KNO_3. — White crystalline salt. Dimorphous. Usual form of crystals orthorhombic prisms, but under certain conditions crystallizes in rhombohedra like $NaNO_3$ (hexagonal). Melts at 339° without decomposition. Is decomposed at a red heat, giving off a mixture of oxygen and nitrogen gases. Deflagrates on glowing coals. Nitre is a natural product, and is chiefly used in the manufacture of gunpowder. It is also employed in curing meat, and the fused salt (sal prunelle) is a useful medicine.

157. **Characteristic Reactions.** — Salts of potassium are distinguished from those of sodium by giving a precipitate with an excess of tartaric acid and with acid platinic chloride.

$$(KCl + \underset{\text{Tartaric Acid.}}{H,H\text{-}C_4H_4O_6} + Aq) = \underset{\text{Acid Potassic Tartrate.}}{\mathbf{H,K\text{=}C_4H_4O_6}} + (HCl + Aq). \quad [107]$$

$$(2\,KCl + PtCl_6H_2 + Aq) = \mathbf{PtCl_6K_2} + (2\,HCl + Aq). \quad [108]$$

158. **LITHIUM, RUBIDIUM, and CÆSIUM** are found in very minute quantities in certain mineral waters, in lepidolite mica, and in a

few other rare minerals. They are always associated with potassium and sodium, to which they are closely allied in all their chemical relations. They form with sodium and potassium a series of electro-positive elements quite as well marked as the series of electro-negative elements of the previous group; and, following the same law, the most electro-positive elements are the lowest in the series, and have the highest atomic weights. Hence, therefore, the chemical energy of the elements of this group, as manifested by the strength of their affinities for elements of the opposite class, like those of the chlorine group, increases as we descend in the series. The metal lithium is remarkable as being the lightest solid known. *Sp. Gr.* = 0.59.

159. **Characteristic Reactions.** — The compounds of each of the five "alkaline metals" impart a peculiar color to the flame of the Bunsen lamp. These colored flames, when examined with the spectroscope, exhibit characteristic bands, by which the elements may be distinguished, and both rubidium and cæsium were discovered by this means. (Chapter XIV.) As an almost universal rule, the simple salts of the "alkaline metals" are soluble in water, and the ready solubility in water both of the hydrates and the carbonates is a very characteristic feature of these elements.

QUESTIONS AND PROBLEMS.

1. What is the theoretical Sp. Gr. of sodium vapor? Ans. 23.

2. What is the weight of 1 litre of sodium vapor at 1,093°, but under the normal pressure? ([12] and § 1.)

Ans. Weight of hydrogen gas under the conditions named, $\frac{1}{2}$ of a crith. Hence, weight of sodium vapor, 4.6 criths, or 0.4121 of a gramme.

3. In the preparation of sodium [92], what weight of metal ought to be obtained from 20 kilo. of sodic carbonate, and how many litres of carbonic oxide gas should be formed for every gramme of sodium obtained?

Ans. 8.680 kilo. of sodium, and 1.446 litres of carbonic oxide.

4. One cubic decimetre of rock-salt contains how many cubic decimetres of metallic sodium, and how many litres of chlorine gas?

Ans. 0.8422 d. m.^{3} of sodium, and 396.5 litres of chlorine.

5. To what extent is the solubility of common salt influenced by the temperature? (Consult Storer's Dictionary of Solubilities, and compare Fig. 2, page 149.)

19. Analyze equations [103, 104, 105, 106], and show that the various symbols are written in conformity to the rules referred to above, No. 15.

20. If a saturated solution of nitre is made at 38°, and subsequently cooled to 10°, what proportion of the salt will crystallize out? (Fig. 2.)

Ans. Two thirds.

21. The difference between the two kinds of soap corresponds to what difference of properties between sodic and potassic carbonate?

Ans. The one effloresces and the other deliquesces in the air.

22. Represent by graphic symbols the constitution of the different potassic oxides.

23. Why would not the salts of sodium be precipitated by the same reagents used in [107 and 108]? Apply the same principle to the interpretation of the other reactions of this section.

DIVISION IV.

160. **SILVER.** $Ag = 108$. — Univalent. Found in small quantities in nature, chiefly in the metallic state, or in combination with chlorine, sulphur, arsenic, or antimony.

161. **Metallic Silver.** $Ag\text{-}Ag$? — *Sp. Gr.* 10.474. Fuses at about 1,000°. The principal ores are

Native Silver	$Ag\text{-}Ag$
Horn Silver	$AgCl$
Silver Glance	Ag_2S
Light-red Silver Ore (Proustite)	$(AgS)_3{=}As$
Dark-red Silver Ore (Pyrargyrite)	$(AgS)_3{=}Sb$

These ores are found chiefly in mineral veins, either by themselves or associated with ores of lead and copper, with which they are frequently smelted, and the silver subsequently separated from the regulus thus obtained. Silver does not oxidize when heated in contact with the air, and for this reason is readily separated from lead in the process of cupellation.

$$xAg_2 . yPb + \tfrac{1}{2}\, yO{=}O = xAg\text{-}Ag + yPbO. \qquad [109]$$

The cupel furnace is so arranged that the melted litharge (PbO) runs off as fast as formed, and leaves the silver pure. Melted silver can dissolve about twenty-two times its volume of oxygen gas; but the gas is given off, in great measure, when the metal solidifies.

162. **Argentic Nitrate.** $AgNO_3$. — The most important soluble salt of silver. Obtained by dissolving silver in dilute nitric acid.

$$3\,Ag\text{-}Ag + (8\,HNO_3 + Aq) = (6\,AgNO_3 + 4\,H_2O + Aq) + 2\,NO. \qquad [110]$$

White crystalline solid which melts at 219°. Fused salt is called lunar caustic, and is much used in surgery as a cautery. Argentic nitrate, although not changed by the light when pure, is readily decomposed when in contact with organic matter, and the black stain of metallic silver thus formed cannot be removed by washing. Hence its application as indelible ink. It is also used in large quantities for hair-dyes, and in the art of photography.

163. **Argentic Chloride.** $AgCl$. — White crystalline solid (Fig. 27). Melts at about 260°, and on cooling forms a horny sectile mass, whence the mineralogical name, Horn Silver. Prepared by adding to a solution of argentic nitrate any soluble chloride.

$$(AgNO_3 + NaCl + Aq) = \mathbf{AgCl} + (NaNO_3 + Aq). \quad [111]$$

We thus obtain a white curdy precipitate, which is insoluble in water or dilute acids, but soluble in ammonia, in potassic cyanide, and in sodic thiosulphite. Owing to a partial reduction, the white powder blackens in the light, especially in the presence of organic matter and an excess of argentic nitrate. On this property is based the ordinary process of photographic printing. In contact with dilute acids, argentic chloride is very readily reduced by metallic zinc.

$$2\,AgCl + Zn = ZnCl_2 + Ag_2. \quad [112]$$

It may also be reduced by hydrogen or hydrocarbon gas passed over the chloride in a heated tube.

$$2\,\mathbf{AgCl} + \mathbf{H\text{-}H} = \mathbf{Ag\text{-}Ag} + 2\,\mathbf{HCl}. \quad [113]$$

In the process of electroplating, argentic chloride, dissolved in an aqueous solution of potassic cyanide, is decomposed by the electric current. (§ 98.)

164. **Argentic Bromide,** $AgBr$, and **Argentic Iodide,** AgI, resemble argentic chloride, and are formed in a similar way. The last, however, has a yellow color, and is insoluble in ammonia. In presence of an excess of argentic nitrate, and after exposure to light, they are at once reduced to the metallic state by solution of ferrous sulphate. Before exposure the reduction takes place very slowly, and on this reaction is based the art of photography. The steps of the process are: 1. Spreading over a glass plate a film of collodion, holding in solution a mixture of metallic bromides and iodides; 2. Immersing the coated plate in a solution of argentic nitrate until a mixture of argentic bromide and iodide is formed in the film; 3. Exposing the plate to light in the camera, where the image formed by a lens falls upon it; 4. Developing the latent image by a solution of ferrous sulphate; 5. Dissolving out the undecomposed silver salt by a solution of sodic thiosulphite.

165. **Argentous Oxide,** Ag_4O, **Argentic Oxide,** Ag_2O, **Argentic Peroxide,** Ag_2O_2. — The second is a brown powder which falls on

adding the solution of an alkaline hydrate to a solution of argentic nitrate. It is very slightly soluble in water, and the solution has an alkaline reaction, and the moist precipitate absorbs CO_2 from the air.

166. **Characteristic Tests.** — Most silver compounds may be reduced to pure silver before the blowpipe; and whenever they are brought into solution the silver can be recognized and the amount very accurately determined by the reaction just given [111]. Silver is remarkable for forming anhydrous salts; and whenever we wish to determine the molecular weight of an acid, it is generally best to analyze its silver salt. (§ 53.)

DIVISION V.

167. **THALLIUM.** $Tl = 204.1$. — Usual quantivalence one, but also trivalent. A very rare element, found in some varieties of pyrites and in Crookesite, a selenide of copper and thallium, from a copper mine in Sweden. The brown oxide of thallium, Tl_2O, is soluble in water, and absorbs CO_2 from the air. It forms a series of salts, most of which are isomorphous with the corresponding salts of potassium, and in many other respects the compounds of this element resemble those of the metals of the alkalies. On the other hand, thallium forms a black sulphide, Tl_2S, insoluble. In this respect, and also in the properties of its haloid compounds, thallium is allied to lead, which it resembles also as a metal. This element differs, however, from lead as much as from the alkaline metals, in forming a sesquioxide, Tl_2O_3, and a class of well-marked sesquioxide salts. It forms, also, a sesquisulphide, Tl_2S_3, and a terchloride, $TlCl_3$. Such are the manifold relations of this element, and it is phenomena of this sort that render any scheme of classifying the chemical elements yet proposed so very unsatisfactory.

The vapor of thallium imparts a green color to the flame of a Bunsen lamp, and shows a single green band in the spectroscope.

QUESTIONS AND PROBLEMS.

1. Given the percentage composition of Proustite, silver, 65.45 ; sulphur, 19.39 ; arsenic, 15.16. Required the symbol. Ans. Ag_3S_3As.

2. How much greater is the per cent of silver in Proustite than in Pyrargyrite? Ans. 5.68 per cent.

3. Draw diagrams illustrating the molecular constitution of the different silver ores.

4. Analyze reaction [110], and point out the difference between it and the class of reactions of which [64] is the type.

5. If a given mass of argentiferous lead contains three fourths of one per cent of silver, how many kilogrammes of litharge will be made in the process of cupellation to each kilogramme of silver extracted, and how many cubic metres of oxygen gas will be absorbed by the process?

Ans. 142.5 kilo. of litharge, and 7.134 $\overline{\text{m.}}^3$ of oxygen.

6. One gramme of silver treated as indicated by [110] and [111] yielded 1.328 grammes of argentic chloride. What is the atomic weight of silver? The atomic weight of chlorine is assumed to be known, 35.5, and also the specific heat of argentic chloride, 0.091. Ans. 108.

7. One gramme of argentic chloride reduced by hydrogen [113] yielded 0.7526 of a gramme of silver. What is the atomic weight of silver? The same values are assumed as in the last problem. Ans. 108.

8. One gramme of argentic oxalate yields when heated 0.7105 gramme of silver. We have reason to believe that oxalic acid is bibasic. What is its molecular weight? (§ 53.) Ans. 90.

9. Write the reaction of a solution of potassic hydrate on a solution of argentic nitrate, and compare this reaction with the corresponding reaction [207].

10. According to Roscoe the **Sp. Gr.** of thallium chloride is 8.2. What evidence does this observation give of the quantivalence of thallium?

DIVISION VI.

168. **OXYGEN.** $O = 16$. — Bivalent. The most abundant and the most widely diffused of the elements. Forms one fifth of the atmosphere, eight ninths of water, more than three fourths of organized beings, and one half of the solid crust of the globe.

169. **Oxygen Gas.** $O{=}O$. — Exists in a free state in the atmosphere, but mixed with nitrogen gas. May be extracted from the air by either of the following double reactions. Metallic mercury or baric oxide is first heated in the air, and then the product of the first reaction raised to a much higher temperature.

$$\begin{array}{ll} 1.\ 2\,Hg + \text{⓪=⓪} = 2\,HgO. & 1.\ 2\,BaO + \text{⓪=⓪} = 2\,BaO_2. \\ 2.\ 2\,HgO = 2\,Hg + \text{⓪=⓪}. & 2.\ 2\,BaO_2 = 2\,BaO + \text{⓪=⓪}. \end{array} \quad [114]$$

Generally obtained from commercial or natural products rich in oxygen, by one of the reactions given below. The materials must in each case be heated to a definite temperature, and the last two reactions require a full red heat.

$$2\,KClO_3 = 2\,KCl + 3\,\text{⓪=⓪}.^{*} \quad [115]$$

$$2\,K_2Cr_2O_7 + 10\,H_2SO_4 = 4\,(HKSO_4) + 2\,([Cr_2]\,3\,SO_4) + 8\,H_2O + 3\,\text{⓪=⓪}. \quad [116]$$

$$2\,MnO_2 + 2\,H_2SO_4 = 2\,MnSO_4 + 2\,H_2O + \text{⓪=⓪} \quad [117]$$

$$3\,MnO_2 = Mn_3O_4 + \text{⓪=⓪}. \quad [118]$$

$$2\,H_2SO_4 = 2\,H_2O + 2\,SO_2 + \text{⓪=⓪}. \quad [119]$$

Also by electrolysis of water and by [66]. Oxygen gas is a chief product of vegetable life. Under the influence of the sun's rays the plants decompose the carbonic acid of their food, fixing the carbon and liberating the oxygen. Oxygen gas manifests intense affinities, but these are only called into play under regulated conditions. (Review Chapter XIII. on Relations of the Atoms to Heat.) When an elementary

* This reaction is greatly facilitated by mixing the potassic chlorate with cupric oxide or manganic dioxide, which, however, undergo in the process no apparent change.

substance unites with oxygen it is said to be *oxidized*, and when the compound is decomposed the oxide is said to be *reduced*.

170. **Oxygen Compounds.** — The most important classes of oxides are illustrated by the following symbols and examples : —

1.	$\overset{I}{R}_2O$	or	$\overset{I}{R},\overset{I}{R}\text{-}O$	as in	H_2O	K_2O	Ag_2O
2.	$\overset{I}{R}_2O_2$	"	$\overset{I}{R},(\overset{I}{R}\text{-}O)\text{-}O$	"	H_2O_2	K_2O_2	Ag_2O_2
3.	$\overset{II}{R}O$	"	$\overset{II}{R}\text{=}O$	"	FeO	CaO	PbO
4.	$\overset{II}{R}_2O$	"	$(\overset{II}{R}\text{-}\overset{II}{R})\text{-}O$	"	Cu_2O	Hg_2O	Pb_2O
5.	$\overset{II}{R}O_2$	"	$(\overset{II}{R}\text{-}O)\text{=}O$	"	MnO_2	BaO_2	PbO_2
6.	$\overset{III}{R}_2O_3$	"	$(\overset{III}{R}\text{-}O\text{-}\overset{III}{R})\equiv O_2$	"	B_2O_3	Au_2O_3	Bi_2O_3
7.	$\overset{IV}{R}O_2$	"	$\overset{IV}{R}\equiv O_2$	"	SnO_2	SiO_2	CO_2
8.	$\overset{IV}{R}_2O_3$	"	$(\overset{IV}{R}\text{-}\overset{IV}{R})\equiv O_3$	"	Fe_2O_3	Al_2O_3	Sn_2O_3
9.	$\overset{II\,\&\,IV}{R_3}O_4$	"	$\overset{II}{R}\text{=}O_2\text{=}[\overset{IV}{R_2}]\equiv O_2$	"	Fe_3O_4	Cr_2O_4	Co_3O_4
10.	$\overset{V}{R}_2O_5$	"	$(\overset{V}{R}\text{-}O\text{-}\overset{V}{R})\equiv O_4$	"	N_2O_5	P_2O_5	As_2O_5
11.	$\overset{V}{R}_2O_4$	"	$(\overset{V}{R}\text{-}\overset{V}{R})\equiv O_4$	"	V_2O_4	Sb_2O_4	Bi_2O_4
12.	$\overset{VI}{R}O_3$	"	$\overset{VI}{R}\equiv O_3$	"	SO_3	SeO_3	MoO_3

As a rule, the oxides of the forms 1 and 3 act as basic anhydrides (§48), and are called protoxides. On the other hand, the oxides of the forms 6, 7, 10, and 12 generally act as acid anhydrides. The oxides of the form 8 are called sesquioxides. They usually act as basic, but sometimes as acid anhydrides, and at other times like the peroxides mentioned below. The oxides of the forms 9 and 11 are very indifferent bodies, and those of the first class are sometimes called saline oxides. The oxides of the forms 2 and 5 are called di- or per-oxides. They act as powerful oxidizing agents, readily giving up one half of the oxygen they contain. [74 and 77.] The oxides of the form 4 are called suboxides. They sometimes act as basic anhydrides, but in most cases when acted on by acids they change into protoxides, either giving up one half of the metal or taking up as much again oxygen as they contain. The relation of the oxides to the acids, bases, and salts has been already explained. (Review Chapters IX. and X.)

Besides the above classes of oxides, all of which comprise actual compounds, there are others, most of which are only known as com-

pound radicals. With many of these radicals the student is already familiar, such as SO_2, SO, NO_2, NO, PO, in all of which the oxygen atoms only satisfy a part of the affinities of the multivalent atoms, with which they are grouped, and the quantivalence of the radical is easily found by Wurtz's rule. (§ 29.)

171. **Ozone.** $(O\text{-}O)''O$. — The best opinion that can at present be formed in regard to the constitution of this remarkable substance is expressed by the rational symbol here given. Ozone is produced under a great variety of conditions, as, — 1. During the passage of electric sparks through air or oxygen. 2. During the electrolysis of water. 3. During the slow combustion of phosphorus in *moist* air. 4. During the slow combustion of alcohol, ether, and volatile oils. 5. By decomposing baric peroxide with sulphuric acid, and by several other similar reactions. Ozone as thus obtained, however, is very largely diluted with air or oxygen gas, and we have not yet succeeded in preparing it in a pure condition. It differs from ordinary oxygen gas, — 1. In being more readily condensed to the liquid state. 2. In having a blue color, which is very marked in the liquid state, and perceptible even in the gas if the layer through which the light passes is one metre thick. 3. In having a peculiar odor, with which we are familiar, as a concomitant of electrical action. 4. In acting as a powerful oxidizing agent at the ordinary temperature of the air. It corrodes cork, india-rubber, and other organic materials. It bleaches indigo. It even oxidizes silver, and displaces iodine from its metallic compounds. If a slip of paper moistened with starch and potassic iodide is inserted in a jar containing the smallest trace of ozone, it is immediately colored blue, owing to the liberation of the iodine (§ 140). In like manner, paper wet with a solution of manganous sulphate is turned brown by ozone, owing to the oxidation of the manganese, and paper stained with plumbic sulphide is bleached by the same agent, because the black sulphide is changed to the white sulphate. 5. In the fact that its Sp. Gr. is 24 instead of 16.

The formation of ozone in a confined mass of oxygen gas is attended with a reduction of volume; and since the ozone thus formed may be absorbed by oil of turpentine, we have thus the means of determining its specific gravity, and the results, if correct, prove that the molecule of ozone consists of three oxygen atoms. Again, during most cases of oxidation by ozone, the volume of the ozonized oxygen does not change, and this fact is consistent with the theory of its constitution which our

molecular formula expresses, as is illustrated by the following reaction: —

$$Ag\text{-}Ag + 2\,(O\text{-}O)\text{-}O = Ag_2O_2 + 2\,O\text{-}O. \qquad [120]$$

It has been shown, however, that oil of turpentine absorbs the molecule of ozone as a whole, and is, therefore, an exception to the general rule.

The metal in the above reaction is raised to the condition of peroxide, and it is probable that several of the oxides and oxygen acids contain one or more atoms of oxygen in the same condition as in ozone. Such compounds have been called ozonides, and among them are classed the peroxides of silver, lead, and manganese, the sesquioxides of nickel and cobalt, as also chromic, manganic, and permanganic acids with their various salts.

The peroxides of hydrogen, barium, strontium, sodium, and potassium decompose the ozonides just mentioned with the evolution of oxygen gas, thus: —

$$(Pb\text{-}O)\text{-}\bar{O} + H,Ho\text{-}\overset{+}{O} = PbO + H_2O + O\text{-}O. \qquad [121]$$

Compare also [75]. Hence, a distinction has been made between ozonides and antozonides, and reactions like [121] have been explained by assuming that the second atom of oxygen in these two classes of peroxides is in an opposite polar state. It has been supposed, also, that there were two corresponding conditions of ozone; but, according to more recent investigations, the so-called antozone was only hydrogen peroxide.

Ozone appears to be constantly present in the atmosphere, and important effects have been attributed to its influence. It has been thought to be the active agent in all processes of slow combustion and decay, and to play an important part in the economy of nature. But although numerous and long-continued observations of the amount of ozone in the atmosphere have been made, the methods employed are not now regarded as trustworthy, or the results of importance. At a temperature of 300° ozone is instantly changed into common oxygen gas, and at a temperature no higher than boiling water it slowly returns to the same condition.

QUESTIONS AND PROBLEMS.

1. What is the reason for writing the symbol of oxygen gas $O=O$? (§§ 18 and 20.)

2. What is the difference between the condition of oxygen gas in the atmosphere and that of the same gas in a pure condition contained in a bell-glass standing over a pneumatic trough?

3. Were the nitrogen gas of the atmosphere removed, would the physical condition of the oxygen gas be changed?

4. If by either of the methods [114] oxygen gas is obtained directly from the atmosphere, how many litres of air would be required to yield one litre of oxygen gas at the same temperature and pressure? (§ 64.)

Ans. 4.77 litres of air.

5. How much potassic chlorate must be used to yield 100 litres of oxygen gas at 30° and 38 c. m. pressure? Ans. 165 grs.

6. What weight of potassic dichromate [116] must be used to yield a litre of oxygen gas, Sp. Gr. = 96? Ans. 52.77 grs.

7. If 32.05 grammes of potassic chlorate are decomposed in a closed vacuous vessel of 1,010 $\overline{\text{c. m.}}^3$ capacity, what will be the tension of the gas in the vessel at 273°? Ans. 131.6 c. m.

8. What weight of oxygen gas is required to fill a globe of 10 litres' capacity at 27°.3 and 38 c. m. pressure? Ans. 6.515 grammes.

9. From a given weight of MnO_2 how much more oxygen gas can be obtained by reaction [117] than by [118]? Ans. $\frac{1}{2}$ more.

10. A volume of air measuring 100 $\overline{\text{c.m.}}^3$ is mixed with 50 $\overline{\text{c.m.}}^3$ of hydrogen gas and exploded. What volume of gas is left, assuming that the volumes are all measured under standard conditions, and that all the water formed is condensed? (§ 64.) Ans. 87.12 $\overline{\text{c.m.}}^3$.

11. In an experiment like the last, with the same initial volume of air and hydrogen, the volume of the residual gas measured 89.41 $\overline{\text{c. m.}}^3$. What is the composition of the air? It is assumed that the volumes are measured under a constant pressure of 76 c. m., and at a temperature at which the tension of aqueous vapor equals 2 c. m.

Ans. 20.96 per cent oxygen, 79.04 nitrogen.

12. Analyze reaction [116], and show from which of the factors the oxygen is derived.

13. Represent reaction [118] by graphic symbols.

14. What volume of chlorine gas is required to decompose one litre of aqueous vapor? Ans. 1 litre.

15. If one gramme of water is decomposed by galvanism in a closed glass globe containing 1.86 litres of air under normal conditions, what will be the tension of the resulting gas mixture, leaving out of the account the tension of the aqueous vapor which may be present. Ans. 152 c. m.

16. Explain the change of color which takes place when paper moistened with a solution of starch and potassic iodide is exposed to the action of ozone.

17. Explain the method of finding the Sp. Gr. of ozone.

18. Can you devise a method of finding the Sp. Gr. of ozone based on the principle of § 63?

19. Explain the reasons for writing the symbol of ozone $(O\text{-}O)\text{=}O$.

DIVISION VII.

172. **SULPHUR.** $S = 32$. — Usually bivalent when in combination with metals or positive radicals, but in other associations frequently quadrivalent and sextivalent. Widely and abundantly distributed in nature, chiefly in combination, forming various metallic sulphides and sulphates. The most abundant of these are iron pyrites, FeS_2, and gypsum, $CaSO_4 . 2\,H_2O$. Found also native in volcanic districts. It is, moreover, an essential, although a very subordinate, ingredient of the animal tissues. Sulphur is very closely allied to oxygen, and, corresponding to each metallic oxide, there is usually a sulphide of the same molecular structure; and, substituting the symbol of sulphur for that of oxygen, the table of oxides on page 310 will serve equally well as a classification of the sulphides.

The greater part of the sulphur of commerce comes from the mines of Sicily, where it is either melted or distilled from the volcanic earth. A small quantity is obtained by roasting or distilling iron pyrites. Common sulphur is a very brittle, yellow solid, melting at 114°, and boiling at 440°, when it forms a dense red vapor. It is insoluble in water, and nearly so in alcohol, ether, and chloroform, but readily soluble in carbonic disulphide, benzol, and oil of turpentine, the solvent power of the last two liquids being greatly increased by heat. Sulphur assumes a great variety of allotropic modifications, which are manifested by differences of crystalline form, specific gravity, solubility, and color. At the ordinary temperature it crystallizes in octahedrons of the orthorhombic system, *Sp. Gr.* 2.05, and above 105° in oblique prisms of the monoclinic systems, *Sp. Gr.* 1.98. Moreover, the one crystalline condition passes into the other at the temperature at which it is normally formed. If heated to 230°, melted sulphur becomes darker-colored, thick, and pasty, and if suddenly cooled the mass remains plastic for some time. At 100° this plastic material suddenly changes back to brittle sulphur, with evolution of heat, and the same change soon follows, although more slowly, at the ordinary temperature. If sulphur is heated to 230° and suddenly cooled several times in succession, it is in part converted into a peculiar dark-colored variety, wholly insoluble in all solvents, and easily separated by carbonic disulphide from the unchanged portion. Moreover, ordi-

nary flowers of sulphur (formed by condensing the vapor of sulphur in *cold* brick chambers) consist in part of a yellow powder, insoluble in carbonic disulphide, which appears to be still another condition of sulphur, and several other modifications, including a black and a red variety, have been described as distinct allotropic states. Sulphur appears, even in the state of vapor, to present differences of condition. Just above its boiling point the Sp. Gr. of sulphur vapor is 96, which corresponds to the molecular formula $S_8 \equiv S_8$; and not until the temperature reaches 1,000° does the Sp. Gr. become 32, corresponding to the formula $S=S$, like that of oxygen gas. Sulphur has strong affinity for the metals, many of which burn in its vapor with great brilliancy. It has also a strong affinity for oxygen. It is very combustible, taking fire at a low temperature, and forming by burning SO_2. It is chiefly used for making sulphuric acid and vulcanizing india-rubber; but it has many subordinate applications both in the arts and in medicine. The so-called milk of sulphur, used in pharmacy, is obtained by dissolving flowers of sulphur in alkaline liquids, and subsequently precipitating with acid.

173. **Hydric Sulphide, Sulphohydric Acid, Sulphuretted Hydrogen,** H_2S. — A colorless gas, which by pressure and cold may be condensed to a limpid, colorless liquid (*Sp. Gr.* = 0.9), boiling at −62°, and freezing at −86°. Is soluble in water and alcohol, one volume of water at 0° dissolving 4.37 volumes, and one volume of alcohol at the same temperature dissolving 17.9 volumes of the gas. Has a repulsive odor, and is a constant product of decaying animal tissues. Generally obtained by the reaction

$$FeS + (H_2SO_4 + Aq) = (FeSO_4 + Aq) + H_2S; \qquad [122]$$

but as the ferrous sulphide commonly used contains more or less metallic iron, the gas thus prepared is mixed with hydrogen. It is obtained in a purer condition from

$$Sb_2S_3 + (6\,HCl + Aq) = (2\,SbCl_3 + Aq) + 3\,H_2S. \qquad [123]$$

Hydric sulphide is very combustible, and burns with a pale blue flame.

$$2\,H_2S + 3\,O=O = 2\,H_2O + 2\,SO_2. \qquad [124]$$

The solution of the gas exposed to the air soon becomes turbid, owing to the oxidation of the hydrogen and consequent separation of sulphur.

$$(2\,H_2S + Aq) + \text{O=O} = (2\,H_2O + Aq) + \text{S=S}. \qquad [125]$$

If the action is assisted by porous solids, the oxidation is more complete.

$$(H_2S + Aq) + 2\,O{=}O = (H_2{=}O_2{=}SO_2 + Aq). \qquad [126]$$

The substance is also decomposed by chlorine, bromine, or iodine.

$$(2\,H_2S + 2\,I{-}I + Aq) = (4\,HI + Aq) + S{=}S. \qquad [127]$$

On this last reaction is based a simple process of determining volumetrically the amount of H_2S in a given solution. The compound may be analyzed by heating metallic tin in a confined volume of the gas.

$$H_2S + Sn = SnS + H{-}H. \qquad [128]$$

Although the sulphur is removed by the tin, the volume of the gas does not change. Hydric sulphide is not unfrequently formed in nature from calcic sulphate, which in contact with decaying animal or vegetable matter loses its oxygen, when the carbonic dioxide of the atmosphere, acting on the resulting calcic sulphide, sets free the compound in question. It is probably thus that the soluble sulphides in many mineral springs originate.

Hydric sulphide is one of the most important chemical reagents, and is used to convert into sulphides various metallic hydrates and other salts.

1. Action on alkaline hydrates.

$$(K{-}O{-}H + H_2S + Aq) = (K{-}S{-}H + H_2O + Aq). \qquad [129]$$

$$(K{-}S{-}H + K{-}O{-}H + Aq) = (K_2S + H_2O + Aq). \qquad [130]$$

Thus may also be formed $Na{-}HS$, $Na_2{=}S$, $NH_4{-}HS$, $(NH_4)_2{=}S$. (§ 38.)

2. Action on salts of the more electro-negative metals.

$$(CdSO_4 + H_2S + Aq) = CdS + (H_2SO_4 + Aq). \qquad [131]$$

So also may be precipitated from *acid* solutions of their salts

As_2S_3,	Sb_2S_3,	Sb_2S_5, (?)	SnS,	SnS_2,	PtS_2,	Au_2S_3,
Yellow.	Red.	Orange.	Brown.	Yellow.	Brown.	Black.

all of which are soluble in alkaline sulphides, and

CdS,	CuS,	Bi_2S_3,	Ag_2S,	HgS,	$[Hg_2]S$,	PbS,
Yellow.	Black.	Black.	Black.	Black.	Black.	Black.

all of which are insoluble in alkaline sulphides.

3. Action on salts of the more electro-positive metals. The following sulphides, although not precipitated from *acid* solutions, are pre-

cipitated when sufficient ammonia is added to neutralize all the acids present, or when an alkaline sulphide is used in place of H_2S: —

$$\underset{\text{White.}}{ZnS}, \quad \underset{\text{Pink.}}{MnS}, \quad \underset{\text{Black.}}{FeS}, \quad \underset{\text{Black.}}{NiS}, \quad \underset{\text{Black.}}{CoS}.$$

At the same time aluminum and chromium are precipitated as hydrates. The remaining common metals, viz. *Ba*, *Sr*, *Ca*, *Mg*, *K*, and *Na*, forming sulphides soluble in water, are not precipitated by H_2S under any conditions. Thus H_2S serves to divide the metallic radicals into groups, and on these relations the ordinary methods of qualitative analysis are based. It will be borne in mind that in these "groups" are sometimes brought together very dissimilar elements, and the grouping rests simply on accidental similarities in the solubility or insolubility, in the same liquids, of the corresponding compounds (sulphides) of the different elements.

4. Action as reducing agent.

$$([Fe_2]Cl_6 + H_2S + Aq) = (2\,FeCl_2 + 2\,HCl + Aq) + S. \quad [132]$$

$$(\underset{\text{Red.}}{K_2Cr_2O_7} + 8\,HCl + 3\,H_2S + Aq = \underset{\text{Green.}}{([Cr_2]Cl_6} + 2\,KCl + 7\,H_2O + Aq) + S_3. \quad [133]$$

$$10\,H_2S + 10\,SO_2 = 5\,S_2 + 8\,H_2O + \underset{\text{Pentathionic Acid.}}{2\,H_2S_5O_6}. \quad [134]$$

174. **Hydric Persulphide**, H_2S_2, analogous to H_2O_2, can be obtained by gradually adding sodic bisulphide to hydrochloric acid. It is a yellow, oily liquid, and very unstable.

175. **Alkaline Sulphides** and **Sulphohydrates.** — Solutions of the simple sulphides and sulphohydrates are best formed as above. These solutions readily dissolve sulphur, and various persulphides are thus formed. The following six sulphides of potassium are known: K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5, and K_2S_6. Other modes of preparing similar compounds are illustrated by the following reactions: —

$$\underset{\text{Ignited in gas current.}}{K_2{=}O_2{=}SO_2} + 4\,H{-}H = K_2S + 4\,H_2O. \quad [135]$$

$$12\,S + (\underset{\text{Boiled in solution.}}{6\,K{-}O{-}H} + Aq) = (\underset{\text{Pentasulphide.}}{2\,K_2S_5} + \underset{\text{Thiosulphite.}}{K_2S_2O_3} + 3\,H_2O + Aq). \quad [136]$$

$$16\,S + 8\,K{-}O{-}H = 3\,K_2S_5 + K_2SO_4 + 4\,H_2O. \quad [137]$$
Melted together at a high temperature.

or
$$8\,S + 3\,K_2{=}O_2{=}CO = 2\,K_2S_3 + K_2S_2O_3 + 3\,CO_2,$$
$$12\,S + 3\,K_2{=}O_2{=}CO = 2\,K_2S_5 + K_2S_2O_3 + 3\,CO_2. \quad [138]$$
Melted together at a lower temperature.

The products of the last two reactions are not constant, but various persulphides are formed, depending on the temperature and the conditions of the process. The resulting mixture is a yellow solid called liver of sulphur. When treated with acids, the various sulphides react as follows: —

$$(K\text{-}HS + HCl + Aq) = (KCl + Aq) + H_2S. \quad [139]$$

$$(K_2S + 2\,HCl + Aq) = (2\,KCl + Aq) + H_2S. \quad [140]$$

$$(K_2S_2 + 2\,HCl + Aq) = (2\,KCl + Aq) + S_2 + H_2S. \quad [141]$$

In general,

$$(K_2S_x + 2\,HCl + Aq) = (2\,KCl + Aq) + S_{x-1} + H_2S. \quad [142]$$

Also,

$$(2\,K_2S_5 + K_2S_2O_3 + 6\,HCl + Aq) = (6\,KCl + SO_2 + H_2O + Aq) + 9\,S + 2\,H_2S. \quad [143]$$

Solutions of the alkaline sulphides or sulphohydrates absorb oxygen from the air, and are thus changed into persulphides and thiosulphites.

$$(8\,NH_4\text{-}S\text{-}H + Aq) + 5\,O\text{=}O = \underset{\text{Colorless solution.}}{} (2\,(NH_4)_2S_2 + 2\,(NH_4)_2S_2O_3 + 4\,H_2O + Aq). \quad [144]$$
Yellow solution.

By further change all the sulphur is eventually oxidized or deposited.

Sulphur and hydric sulphide react on the alkaline earths in nearly the same ways as on the alkalies.

$$CaO + H_2S = CaS + H_2O. \quad [145]$$
Ignited in gas current.

$$CaSO_4 + 4\,H\text{-}H = CaS + 4\,H_2O. \quad [146]$$
Ignited in gas current.

$$CaSO_4 + 4\,C = CaS + 4\,CO. \quad [147]$$
Ignited together.

$$2\,CaS + H_2\text{=}O_2\text{=}H_2 = Ca\text{=}S_2\text{=}H_2 + Ca\text{=}O_2\text{=}H_2. \quad [148]$$
Mixed with water.

$$Ca\text{=}O_2\text{=}H_2 + 2\,H_2S + Aq = (Ca\text{=}S_2\text{=}H_2 + 2\,H_2O + Aq). \quad [149]$$
Passing H_2S through milk of lime.

By boiling sulphur with milk of lime, a mixture of calcic thiosulphite with various calcic persulphides is obtained, among which may be distinguished CaS_2 and CaS_5. By melting together sulphur and calcic hydrate or carbonate, there results a mixture of calcic sulphide and calcic sulphate. If pulverized charcoal is also added, the product is chiefly calcic sulphide, as in "black-ball" (§ 144).

The residue from the lixiviation of black-ball, consisting largely of

calcic sulphide, when exposed to air and moisture, undergoes oxidation similar to [144], and on this has been based a process for recovering the sulphur consumed in the alkali manufacture. Compare § 178.

176. **Compounds of Sulphur and Oxygen.** — The following are known : —

Hyposulphurous Oxide	S_2O_2
Hyposulphurous Acid	H_2O_2S
Sulphurous Oxide	SO_2
Sulphurous Acid	H_2O_2SO
Thiosulphurous Acid	$H_2O_2(S\text{-}O\text{-}S)$
Sulphuric Oxide	SO_3
Sulphuric Acid	$H_2O_2SO_2$
Nordhausen Acid	$H_2O_2(SO_2\text{-}O\text{-}SO_2)$
Dithionic Acid	$H_2O_2(SO_2\text{-}SO_2)$
Trithionic Acid	$H_2O_2(SO_2\text{-}S\text{-}SO_2)$
Tetrathionic Acid	$H_2O_2(SO_2\text{-}S\text{-}S\text{-}SO_2)$
Pentathionic Acid	$H_2O_2(SO_2\text{-}S\text{-}S\text{-}S\text{-}SO_2)$

177. **Sulphurous Oxide.** SO_2. — Colorless gas, having a familiar suffocating odor. It is easily condensed to a colorless liquid, boiling at $-10°$ and freezing at $-76°$; **Sp. Gr.** = 1.49. Natural product of volcanic action, and abundantly evolved during the roasting of copper pyrites and other sulphurous ores. May be prepared by either of the following reactions : —

$$S\text{-}S + 2\,O\text{=}O = 2\,SO_2. \qquad [150]$$
Burning.

$$2\,H_2SO_4 + Hg = HgSO_4 + 2\,H_2O + SO_2. \qquad [151]$$

$$2\,H_2SO_4 + C = 2\,SO_2 + CO_2 + 2\,H_2O. \qquad [152]$$

$$S\text{-}S + MnO_2 = MnS + SO_2. \qquad [153]$$

May be decomposed by the reactions

$$2\,SO_2 + 4\,H\text{-}H = 4\,H_2O + S\text{-}S. \qquad [154]$$

$$SO_2 + 3\,H\text{-}H = 2\,H_2O + H_2S. \qquad [155]$$

The first reaction is obtained by passing a mixture of the two gases through a red-hot tube; the second, by adding to the solution containing SO_2 a small amount of hydrochloric acid with a few pieces of zinc. The H_2S may be detected by a strip of paper moistened with a solution of acetate of lead, and the reaction gives us the means of discovering small quantities of SO_2.

Sulphurous anhydride is a powerful reducing agent. Thus

$$(\underset{\text{Iodic Acid.}}{2\,HIO_3} + 5\,SO_2 + 4\,H_2O + Aq) = (I\text{-}I + 5\,H_2SO_4 + Aq). \quad [156]$$

$$(As_2O_5 + 2\,SO_2 + 2\,H_2O + Aq) = (As_2O_3 + 2\,H_2SO_4 + Aq). \quad [157]$$

$$(SO_2 + I\text{-}I + 2\,H_2O + Aq) = (H_2SO_4 + 2\,HI + Aq). \quad [158]$$

$$(2\,SO_2 + 2\,H_2O + Aq) + \text{⓪=⓪} = (2\,H_2SO_4 + Aq). \quad [159]$$

$$\mathbf{PbO_2 + \text{ⓈⓄ}_2 = PbSO_4}. \quad [160]$$

It is also a powerful disinfecting and antiseptic agent, and is much used for retarding fermentation and putrefaction. It also bleaches some of the more fugitive colors, but the effect is frequently transient, and the reaction not well understood.

178. **Sulphites.** — At 0° water absorbs 68.8 times its bulk of SO_2, and three crystalline hydrates have been described, one of which has the composition $SO_2 . H_2O$, and has been regarded as sulphurous acid, but this opinion may be questioned. The aqueous solution acts in all its physical relations like the simple solution of a gas. Nevertheless, in its chemical relations it acts like an acid, and yields, with many of the metallic oxides, hydrates, or carbonates, a numerous class of salts called the sulphites. The following examples will illustrate their general composition: —

Hydro-sodic Sulphite	$H\text{-}Na\text{-}O_2\text{-}SO . 4\,H_2O$
Disodic Sulphite	$Na_2\text{-}O_2\text{-}SO . 7\,H_2O$
Calcic Sulphite	$Ca\text{-}O_2\text{-}SO$

The sulphites are generally best prepared by transmitting a stream of SO_2 through water in which the metallic oxide, hydrate, or carbonate is suspended. The alkaline salts are the only sulphites which are freely soluble in water. The sulphites of barium, strontium, and calcium dissolve to some extent in water charged with SO_2, and in this respect the sulphites resemble the carbonates. Argentic sulphite, which may be readily obtained by precipitation, undergoes a remarkable reaction when boiled with water.

$$Ag_2\text{-}O_2\text{-}SO + (H_2O + Aq) = Ag\text{-}Ag + (H_2\text{-}O_2\text{-}SO_2 + Aq). \quad [161]$$

178ª. **Thiosulphites.** — Thiosulphurous acid has never been isolated; but several thiosulphites may be obtained by passing a stream of SO_2 through solutions of the corresponding sulphides, or by digesting a solution of the sulphite on powdered sulphur.

$$\mathbf{S} + (Na_2\text{-}O_2\text{-}SO + Aq) = (Na_2\text{-}O_2\text{-}(S\text{-}O\text{-}S) + Aq). \quad [162]$$

Calcic thiosulphite is formed spontaneously in large quantities, both in the refuse lime taken from the purifiers of the gas-works, and in the refuse after the lixiviation of the black-ball at the alkali works, and from this source sodic thiosulphite is now obtained. It is the only thiosulphite of practical value, and is not only used in photography, but also for removing the last traces of chlorine from the bleached pulp used in paper-making, and in the treatment of silver ores.

179. **Hyposulphurous Acid.** — The thiosulphites were formerly named hyposulphites, and are still so called both in commerce and in the arts. But according to the rules for chemical nomenclature we have proposed (§ 52), the term hyposulphurous acid appropriately belongs to the ortho-acid, $H_2^{\prime\prime}O_2^{\prime\prime}S$, in which sulphur is bivalent. This acid is obtained by the action of metallic zinc or iron on sulphurous acid in a closed vessel. The hydrogen evolved by the action of the metal on the acid determines with another portion of the sulphurous acid the following reaction :

$$H_2SO_3 + H_2 = H_2O_2S + H_2O. \qquad [163]$$

A deep yellow-colored liquid is thus obtained, possessing powerful reducing properties. It bleaches organic colors more quickly than sulphurous acid, and precipitates silver and mercury from solutions of their salts.

$$HgCl_2 + H_2O_2S + H_2O = Hg + 2HCl + H_2SO_3.$$

Acid sodic hyposulphite is prepared by the action of zinc on acid sodic sulphite.

$$3HNaSO_3 + Zn = H,Na''O_2''S + Na_2SO_3.ZnSO_3 + H_2O. \qquad [164]$$

The products are separated by crystallization. Acid sodic hyposulphite forms colorless crystals, which, when moist, absorb oxygen from the air rapidly, and change into sodic sulphite. A solution of the salt is now much used by the dyer and calico-printer for reducing indigo.

180. **Sulphuric Oxide.** SO_3. — Soft, white, silky-looking crystalline solid, melting at 25°, and volatilizing at 35°. May be obtained either by distillation from the Nordhausen acid, or from sodic disulphate, or else by passing a mixture of SO_2 and $O{=}O$ through a heated tube filled with platinum sponge.

$$H_2''O_2''(SO_2'{-}O{-}SO_2) = H_2''O_2''SO_2 + \mathbb{SO}_3. \qquad [165]$$

$$Na_2''O_2''(SO_2'{-}O{-}SO_2) = Na_2''O_2''SO_2 + \mathbb{SO}_3. \qquad [166]$$

$$2\mathbb{SO}_2 + \mathbb{O}{=}\mathbb{O} = 2\mathbb{SO}_3. \qquad [167]$$

It unites with many metallic oxides to form sulphates, and baryta burns in its vapor.

$$BaO + SO_3 = BaO,SO_3. \qquad [168]$$

It has an intense affinity for water, and the heat developed by the union is so great that the solid hisses like red-hot iron when dropped into the liquid. The product is common sulphuric acid.

181. **Sulphurylic Chloride.** SO_2Cl_2. — May be formed by the direct union of SO_2 and $Cl\text{-}Cl$ under the influence of the sunlight; also by the reaction

$$H_2SO_4 + 2\,PCl_5 = SO_2Cl_2 + 2\,PCl_3O + 2\,HCl. \qquad [169]$$

The product is a liquid boiling at 80°; *Sp. Gr.* 1.68. Slowly decomposed by water.

$$SO_2Cl_2 + 2\,H_2O = H_2SO_4 + 2\,HCl. \qquad [170]$$

There have also been described the allied compounds $H\text{-}O\text{-}SO_2\text{-}Cl$ and SO_2Br_2. The relations of these compounds to sulphuric acid will be made more evident by writing the symbols thus: —

$$Ho_2{=}SO_2, \qquad Ho,Cl{=}SO_2, \qquad Cl_2{=}SO_2, \qquad Br_2{=}SO_2.$$

182. **Sulphuric Acid.** $H_2{=}O_2{=}SO_2$ or $Ho_2{=}SO_2$. — The following reactions are interesting as illustrating the constitution of this important acid, although of no practical value as methods of making it: —

$$Ho\text{-}Ho + SO_2 = Ho_2{=}SO_2. \qquad [171]$$

$$H_2O + SO_3 = H_2O,SO_3. \qquad [172]$$

$$2\,H_2{=}O_2{=}SO + O{=}O = 2\,H_2{=}O_2{=}SO_2. \qquad [173]$$

$$S{=}S + 4\,H\text{-}O\text{-}NO_2 = 2\,H_2{=}O_2{=}SO_2 + 4\,NO. \qquad [174]$$

For the uses of the arts the acid is made in enormous quantities by burning sulphur, or, more commonly, iron pyrites in suitable ovens or kilns, and conveying the SO_2 thus formed, together with steam and nitric acid fumes, generated simultaneously, into large chambers lined with sheet lead.

1. $$SO_2 + 2\,HNO_3 = H_2SO_4 + 2\,NO_2. \qquad [175]$$

2. $$3\,NO_2 + H_2O = 2\,HNO_3 + NO. \qquad [176]$$

3. $$2\,NO + O{=}O = 2\,NO_2. \qquad [177]$$

These reactions may be repeated indefinitely, and it is evident that the same quantity of nitric acid would serve to convert an indefinite amount of SO_2 into H_2SO_4, were it not for the loss occasioned by the constant draft of air through the chambers. The reaction consists essentially in a transfer of oxygen from the air to the SO_2, the nitrogen compounds acting as the mediator, and the draft yields the requisite supply of oxygen gas. When the amount of aqueous vapor is insufficient, there forms in the chambers a white crystalline compound of somewhat uncertain composition, but to which has been assigned the symbol $(NO_2)_2{}^{v}(SO_2{}^{v}\text{-}O\text{-}SO_2)$. When mixed with water, this compound breaks up into sulphuric acid and nitrous anhydride, so that the formation of the acid may also be represented by the following equations, which are thought by some chemists to represent the process more accurately than those given above:—

1. $$SO_2 + 2\,HoNO_2 = Ho_2SO_2 + 2\,NO_2. \qquad [178]$$

2. $$4\,NO_2 + 4\,SO_2 + O\text{-}O = 2(NO_2)_2{}^{v}(SO_2{}^{v}\text{-}O\text{-}SO_2). \qquad [179]$$

3. $$(NO_2)_2{}^{v}(SO_2{}^{v}\text{-}O\text{-}SO_2) + 2\,H_2O = 2\,Ho_2SO_2 + N_2O_3. \qquad [180]$$

4. $$3\,N_2O_3 + H_2O = 2\,HoNO_2 + 4\,NO. \qquad [181]$$

5. $$2\,NO + O\text{-}O = 2\,NO_2. \qquad [182]$$

The acid drawn from the chambers is very dilute, and for most uses must be concentrated by evaporation, which is begun in leaden pans, but completed in retorts of glass or platinum. The strongest acid thus obtained corresponds to the symbol H_2SO_4. It is an oily liquid (oil of vitriol), *Sp. Gr.* = 1.842, boiling at 327°, and crystallizing at a low temperature. If during the evaporation the temperature is limited to 205°, an acid is obtained of the composition $H_2SO_4 \cdot H_2O$, and *Sp. Gr.* 1.78, which crystallizes at 9°, and by limiting the temperature to 100°, still a second definite hydrate may be obtained, $H_2SO_4 \cdot 2H_2O$, which has *Sp. Gr.* = 1.62. Oil of vitriol may be mixed with water in any proportion, and the hydration of the acid is accompanied by a condensation of volume and a great evolution of heat, the maximum of condensation and the maximum of heat being attained when the proportions are such as to form the second hydrate. A definite *Sp. Gr.* corresponds to each degree of dilution, and tables have been prepared which, when the specific gravity is known, the strength of the acid be determined. The short table which follows gives all the data ired for the problems in this book.

Per Cent of H_2SO_4.	Sp. Gr. at 15°.	Per Cent of SO_3.	Per Cent of H_2SO_4.	Sp. Gr. at 15°.	Per Cent of SO_3.
100	1.8426	81.63	50	1.3980	40.81
95	1.8376	77.55	45	1.3510	36.73
90	1.8220	73.47	40	1.3060	32.65
85	1.7860	69.38	35	1.2640	28.57
80	1.7340	65.30	30	1.2230	24.49
75	1.6750	61.22	25	1.1820	20.40
70	1.6150	57.14	20	1.1440	16.32
65	1.5570	53.05	15	1.1060	12.24
60	1.5010	48.98	10	1.0680	8.16
55	1.4480	44.89	5	1.0320	4.08

In consequence chiefly of its strong attraction for water, sulphuric acid disorganizes and blackens both animal and vegetable tissues. It is also used as a hygroscopic agent, and, under limited conditions, for the dehydration of various chemical compounds. Its action on different chemical agents has been already repeatedly illustrated. See [64, 151, and 266]. It forms several classes of salts, as is illustrated by the following examples: —

Hydro-sodic Sulphate,	$Ho,(NaO)=SO_2$
Disodic Sulphate,	$(NaO)_2=SO_2$ and with $10\,H_2O$
Disodic Disulphate,	$(NaO)_2=(SO_2-O-SO_2)$
Cupric Sulphate,	$CuO_2=SO_2\,.\,5\,H_2O$
Ferrous Sulphate,	$FeO_2=SO_2\,.\,7\,H_2O$
Potassio-ferrous Disulphate,	$FeO_2=(SO=O_2=SO)=(KO)_2\,.\,6\,H_2O$
Aluminic Sulphate,	$Al_2O_6\equiv(SO_2)_3\,.\,18\,H_2O$
Common Alum,	$(KO)_2=(SO_2)_4\equiv Al_2O_6\,.\,24\,H_2O$
Zincic Sulphate,	$ZnO_2=SO_2$
Dizincic Sulphate,	$(ZnO_2)_2\equiv SO$
Trizincic Sulphate,	$(ZnO_2)_3\equiv S$

The last may be regarded as an orthosulphate, but salts of this class are wholly exceptional.

The manufacture of sulphuric acid is one of the most important branches of industry in a civilized community, as there is hardly an art or a trade into which, in some form or other, it does not enter.

183. **Nordhausen Sulphuric Acid**, $Ho_2=(SO_2-O-SO_2)$, corresponding to the disulphates in constitution, may be prepared by dissolving SO_3 in H_2SO_4, and has been manufactured for many years at the

German town whence it takes its name, by the distillation of ferrous sulphate. It may almost be regarded as a solution of SO_3 in H_2SO_4, and the usual product contains a very variable proportion of the anhydride; in fact, a product consisting chiefly of SO_3 is now an article of commerce.

184. **Sulphurous Chloride.** S_2Cl_2. — A yellow, volatile, fuming liquid, formed by distilling sulphur in an atmosphere of chlorine gas. It is a powerful sulphur solvent, and has been used for vulcanizing india-rubber. It is decomposed by water, but mixes with benzol and carbonic disulphide. Sulphuric chloride, SCl_2, and several oxychlorides of sulphur are also known.

185. **SELENIUM**, $Se = 79.4$, **and TELLURIUM**, $Te = 128$. — Two very rare elements, closely allied to sulphur, but presenting such differences as might be anticipated in elements of the same chemical series. They form compounds with hydrogen, H_2Se and H_2Te, analogous to H_2S, and compounds with oxygen and hydrogen resembling sulphurous and sulphuric acids.

Selenium, which follows in the series next to sulphur, manifests its relationship in many ways. The elementary substance, which in its ordinary condition is a brittle solid, having a glassy fracture and a dark brown color, *Sp. Gr.* 4.3, may be obtained in several allotropic states, and in one of these, when its *Sp. Gr.* = 4.8, it has the same monoclinic form and molecular volume as the corresponding condition of sulphur. It readily melts at a varying temperature above 100°, depending on its condition, and at 700° is converted into a deep yellow vapor, which has been observed to have, at a high temperature, Sp. Gr. = 82. It burns in the air with a blue flame, forming chiefly SeO_2, and emits an offensive odor resembling putrid horseradish. Hydric selenide, also, is a gas with a disgusting smell, which, like H_2S, precipitates many of the metals from solutions of their salts as selenides. Selenic acid is a thick oily liquid like sulphuric acid, and many of the selenates cannot be distinguished by merely external characters from the corresponding sulphates. Selenium, moreover, is almost invariably found in nature associated with sulphur, and is extracted from the residues resulting from the treatment of sulphur ores. There are, however, a few rare minerals, which consist mainly of metallic selenides. Among the most important of these may be named Clausthalite, $PbSe$, Berzelianite, $CuSe$, Naumannite, Ag_2Se, and Onofrite, $HgSe$.

When we descend in the series to Tellurium, we find more marked differences. The elementary substance has a silver-white color, a bright metallic lustre, and outwardly resembles a metal. It is closely allied in many of its physical properties to bismuth. It crystallizes in rhombohedrons, and the mineral Tetradymite has been regarded as an isomorphous mixture of native tellurium with native bismuth. Its *Sp. Gr.* = 6.2, and its atomic volume is very much nearer that of bismuth and antimony than that of selenium and sulphur. Nevertheless, in other relations it is closely allied to selenium. It is hard and brittle, a poor conductor of heat and electricity. It fuses between 425° and 475°, and at a high temperature yields a yellow vapor, which has a specific gravity corresponding to the molecular formula $Te=Te$. When heated in the air, it burns with a greenish blue flame, and is converted into tellurous anhydride, TeO_2. Lastly, hydric telluride resembles closely hydric selenide, and the salts of tellurous and telluric acids are similar to the corresponding selenites and selenates; but telluric acid does not, like selenic acid, form salts corresponding to the alums, and its salts are less stable. Tellurium is the chief constituent of a few native compounds, which are highly prized as minerals. Besides Tetradymite, Bi_2Te_3, we have Hessite, Ag_2Te, Sylvanite, $AgAuTe_4$, Altaite, $PbTe$, and Nagyagite, which is a sulphotelluride of lead and gold of somewhat uncertain composition. The elements of this group form then, evidently, a very well marked series, in which, as in the chlorine series, the chemical energy diminishes as the atomic weight increases.

DIVISION VIII.

186. **MOLYBDENUM.** $Mo = 96$. — One of the rarer elements, but not unfrequently met with in the mineral kingdom, usually in combination with sulphur, forming the mineral Molybdenite, MoS_2, which so closely resembles foliated graphite that the two might easily be mistaken for each other. From this mineral we readily obtain by roasting, at a low red heat in a current of air, molybdic anhydride, MoO_3, which is the most characteristic compound of the element. When pure, the anhydride is a pale buff-colored powder, fusing to a straw-colored glass at a red heat, and volatilizing at a higher temperature. It is only sparingly soluble in water, but readily dissolves in ordinary acids, in aqua ammonia, and in solutions of the alkaline hydrates or carbonates, and forms with metallic oxides a numerous class of salts called molybdates. Plumbic molybdate (Wulfenite), $Pb''O_2''MoO_2$, is sometimes found in beautiful yellow or red crystals associated with other lead ores, and ammonic molybdate, $(NH_4)_2''O_2''MoO_2$, is much used in the laboratory as a test for phosphoric acid. Besides MoO_3, the element also forms compounds with one and with two atoms of oxygen, MoO and MoO_2, which act as basic anhydrides; and there is also an intermediate oxide, Mo_2O_5. In solutions of molybdic acid or of molybdates, when acidified with hydrochloric acid, H_2S gives a brownish-black precipitate of MoS_3, and there is still a third sulphide, MoS_4, which, as well as the last, acts as a sulphur acid. There are four chlorides, $MoCl_2$, Mo_2Cl_5, $MoCl_4$, $MoCl_5$. The elementary substance is a brittle silver-white metal ($Sp.\ Gr. = 8.6$), which is unalterable in the air, and very infusible. It can be obtained without difficulty by reducing the oxides with charcoal or hydrogen, but unless the temperature is very high the metal is left as a gray powder. The name is from the Greek, and signifies "a mass of lead."

Molybdenum is remarkable for the great number, as well as for the great complexity, of its compounds. They apparently indicate that the element may have several degrees of quantivalence, both odd and even (§ 28), but the investigation of the molecular structure of these bodies presents great difficulties, and no certain conclusion on this subject can yet be drawn. The same remarks apply to the closely

allied element tungsten, and it is not possible to give an adequate idea of the complex relations of these elements in a few words.

When acid solutions of the molybdates are acted on by reducing agents, as, for example, by $SnCl_2$, certain blue or green products result, and the accompanying change of color serves as a very striking test for molybdenum.

187. **TUNGSTEN.** $W = 184$. — This element occurs in tolerably large quantities combined with calcium in the mineral Scheelite, $CaWO_4$, and with both iron and manganese in Wolfram, of which there are two varieties, $2\,FeWO_4 + 3\,MnWO_4$ and $4\,FeWO_4 + MnWO_4$. Both minerals are decomposed by acids, and by this means we readily obtain tungstic oxide, WO_3, a yellow powder insoluble in water and acids, but readily dissolving in ammonia and solutions of alkaline hydrates, and, when heated with solutions of alkaline carbonates, decomposing the salts with effervescence. From a boiling alkaline solution of tungstic oxide the common acids throw down a yellow precipitate of tungstic acid, H_2WO_4. This acid forms with bases a numerous class of salts called tungstates, which, although of little practical importance, are theoretically very interesting, and have been the object of careful investigation. There are several (at least two) distinct types of these salts, and there are also two modifications of tungstic acid; for, besides the ordinary insoluble condition, both molybdic and tungstic acids have been obtained in a colloidal condition, in which they are very soluble in water (§ 61). The tungstates have the same crystalline form as the corresponding molybdates, and a tungstate of lead, isomorphous with Wulfenite, is a well-known mineral called Scheeltine. Besides WO_3, there is an oxide, WO_2, which also acts as an acid anhydride, and there is also an intermediate oxide of a splendid blue color, which may be produced by the action of reducing agents on the anhydride or on the soluble tungstates. Tungsten is not, like molybdenum, precipitated by H_2S, but the sulphide, WS_2, has been prepared artificially, and resembles very closely the native molybdenite. There is also a sulphide, WS_3, and there are four chlorides, WCl_2, WCl_4, WCl_5, and WCl_6, the last two of which are volatile. The metal itself (*Sp. Gr.* 19.2) is easily reduced, but, in consequence of its great infusibility, cannot be obtained in a compact state except at a very high temperature. It has an iron-gray color, and, when alloyed with steel to the extent of eight or ten per cent, renders the metal exceedingly hard. The compounds neither of tungsten

nor of molybdenum have found any important applications in the arts, although sodic tungstate has been used, mixed with starch, in finishing cambrics, because it has been found to render these light fabrics less inflammable. The name Tungsten had a Swedish origin, and signifies in the original "heavy stone."

QUESTIONS AND PROBLEMS.

1. What is the per cent of sulphur in Gypsum and Iron Pyrites?
Ans. 18.6 per cent and 53.33 per cent.

2. Write the symbols of the different classes of sulphides.

3. Express by graphic symbols the constitution of the various sulphur radicals.

4. What are the atomic volumes of the two crystalline varieties of sulphur? Ans. 15.60 and 16.16.

5. By heating 10.000 grammes of silver in the vapor of sulphur, Dumas obtained 11.4815 grammes of argentic sulphide. What is the atomic weight of sulphur? What assumption is made in your calculation, and what ground have you for this assumption? Ans. 32.000.

6. What is the specific gravity of H_2S gas referred to hydrogen and to air? Ans. 17 and 1.1764.

7. What weight of sulphur is contained in one litre of H_2S?
Ans. 1.434 grammes.

8. How much antimonious sulphide is required for the preparation of one litre of hydric sulphide? How much to prepare 340 grammes?
Ans. 5.076 grammes, 1133.33 grammes.

9. What volume of oxygen gas is required to burn one litre of H_2S, and what are the volumes of the aeriform products?
Ans. $1\frac{1}{2}$ litres of oxygen gas, one litre of aqueous vapor, and one of sulphurous oxide.

10. One litre of $(H_2S + Aq)$ saturated at 0° will absorb what volume of oxygen gas, and will yield what weight of sulphur?
Ans. 2.185 litres, 6.263 grammes.

11. Assuming that a solution of iodine in a solution of potassic iodide has been prepared of known strength, how may this be used to measure the quantity of H_2S in a mineral water?

12. The specific gravity of hydric sulphide has been found by experiment to be 17.2, and by reaction [128] it is shown that any volume of the gas contains an equal volume of hydrogen. Show that these results agree quite closely with the molecular symbol assigned to the compound. How do you explain the slight discrepancy?

13. Write the reactions by which hydric sulphide is formed from calcic sulphate.

14. Write the reaction by which NH_4-HS may be formed from aqua ammonia.

15. Write the reaction of H_2S gas on a solution of plumbic acetate, and calculate what volume of $(H_2S + Aq)$ saturated at 0° would be required to precipitate 0.207 gramme of lead. Ans. 5.109 $\overline{\text{c. m.}}^3$ of $(H_2S + Aq)$.

16. Write the reaction of H_2S on a solution of acetate of zinc. What inference would you draw from the fact that Zn is precipitated by this reagent from an acetic acid solution, while Fe and Mn are not?

17. Into what groups may the metallic radicals be divided by means of the two reagents hydric sulphide and ammonic sulphide, and how must the reagents be used in order to separate these groups from a given solution?

18. In reducing 28 grammes of iron from the condition of ferric to that of ferrous chloride, how much sulphur is precipitated? Ans. 8 grammes.

19. Analyze the reactions [133] and [134], and show how the H_2S gas acts as a reducing agent in each case.

20. Write the reaction of hydrochloric acid on sodic bisulphide.

21. Represent by graphic symbols the constitution of the various potassic sulphides.

22. Analyze reactions [135] to [149].

23. Write the reaction when sulphur and milk of lime are boiled together, assuming first that CaS_2, and secondly that CaS_5 is produced.

24. Write the reaction when sulphur and calcic hydrate are melted together, assuming that CaS_5 and $CaSO_4$ are produced.

25. Represent by graphic symbols the composition of the compounds of sulphur and oxygen. Draw up a scheme showing the relations of the various acids and anhydrides, similar to that of § 131.

26. Is the quantivalence of sulphur in the sulphites and hyposulphites the same as in the sulphates, &c.? Write the graphic symbols of all these compounds on the theory that sulphur is invariably bivalent.

27. What volume of sulphurous oxide would be formed by burning 2.8672 grammes of sulphur? Ans. 2 litres.

28. It has been observed that when sulphur burns in oxygen the volume of the product is the same as the initial volume of oxygen gas. It has been found by experiment that the Sp. Gr. of sulphurous oxide equals 32.28. How do these facts correspond with the molecular symbol usually assigned to the compound? What is the **Sp. Gr.** of SO_2? Ans. 2.234.

29. How much mercury is required to make one litre of SO_2?
Ans. 8.96 grammes.

30. Leaving out of view the value of the mercury used, as it may be easily recovered, by which of the two reactions [151] and [152] may SO_2 be most profitably prepared?

31. How much MnO_2 would be required to yield by reaction [153] sufficient SO_2 to neutralize 1.29 grammes of sodic carbonate?
Ans. 1.059 grammes.

32. Point out the volumetric relations in reaction [154].

33. Are the conditions under which the reaction [155] is obtained in any way peculiar?

34. Compare reactions [157] and [158], and inquire whether a method of volumetric analysis based upon them might not be devised.

35. Represent by graphic symbols the sulphites whose symbols are given in [178].

36. The refuse lime of the gas and alkali works contains calcic disulphide, CaS_2. In what way would this be changed by exposure to the air into calcic thiosulphite, and how from this product could sodic thiosulphite be prepared?

37. Write the reaction of hydrochloric acid on sodic thiosulphite, knowing that thiosulphurous acid, when liberated, yields sulphurous oxide and sulphur.

38. The specific gravity of the vapor of sulphuric oxide has been found by experiment to be 39.9. How does this agree with the theoretical value? Compare the densities of $O=O$, SO_2, and SO_3 as regards the relative degree of condensation in each.

39. What are the relations of the compounds SO_2Cl_2, SO_2ClHO, SO_3, and H_2SO_4 to one another?

40. Analyze the two sets of reactions [175 *et seq.*] and [178 *et seq.*], and show whence the oxygen required to oxidize the sulphurous oxide is derived, and what part the oxides of nitrogen play in the process.

41. In the process of making oxygen gas from sulphuric acid, whence is the oxygen in the first instance derived? Might not the same quantity of acid be made to yield an indefinite supply of gas?

42. It appears by experiment that the Sp. Gr. of H_2SO_4 vapor is 24.42. How does this agree with theory, and how do you explain the discrepancy?

43. It has been found by exact experiments that 100 parts of lead yield 146.45 parts of plumbic sulphate. What is the molecular weight of sulphuric acid? What assumption does your calculation involve (§ 53)? Why do you regard this result as more trustworthy than that of the last problem? Ans. 98.16.

44. How do the symbols of the hydrates of sulphuric acid compare with those of the crystalline salts of this acid?

45. Write the symbols of sulphuric acid and its two hydrates, representing them as compounds of SO_2 with hydroxyl. Point out the distinction between the ortho and meta acids, and show that a similar distinction may be made among the salts.

46. How many litres of sulphuric acid, *Sp. Gr.* 1.615, can be made from 1,000 kilo. of pyrites, assuming that all the sulphur in the mineral is burnt? Ans. 1444.4 litres.

47. How much sulphuric acid by weight, *Sp. Gr.* 1.501, will be required, — 1st. To neutralize 53 grammes of sodic carbonate? 2d. To dissolve 32.6 grammes of zinc? 3d. To precipitate completely 2.08 grammes of baric chloride? Ans. 81.666 grammes, 81.666 grammes, 1.633 grammes.

48. Represent the constitution of the various sulphates by graphic symbols.

49. In what does the symbol of dizincic sulphate differ from that of a sulphite?

50. If the specific gravity and molecular weight of a solid substance be given, how can you find the molecular volume of the substance in the solid condition?

51. How does the molecular volume of sulphur compare with that of selenium, — 1st. In the solid condition? 2d. In the crystalline condition?

52. What is true of the molecular volumes of all substances in the state of gas?

53. Compare the molecular volumes of tellurium and bismuth.

54. What are the analogies, and what are the chief points of difference, between sulphur, selenium, and tellurium?

55. Write the reaction of hydric selenide on a solution of plumbic acetate; also that of potassic selenate on a solution of baric chloride.

56. Write the reaction when Molybdenite is roasted in the air.

57. Write the reaction of H_2S on a solution of molybdic acid in hydrochloric acid.

58. What is the relative proportion of tungstic anhydride in the two varieties of Wolfram? Ans. 76.47 to 76.38%.

59. Write the reaction of hydrochloric acid on Scheelite.

60. In what respects does tungsten resemble molybdenum?

DIVISION IX.

188. **CALCIUM.** $Ca = 40$. — Bivalent. One of the most abundant and important constituents of the crust of the globe. The elementary substance is a soft, malleable metal, with a reddish tinge of color. Readily tarnishes in the air, and burns when heated, forming lime. Decomposes water at all temperatures, forming calcic hydrate.

$$2\,\mathbf{Ca} + \mathbf{O{=}O} = 2\,\mathbf{CaO}.$$
$$Ca + 2\,H_2O = 2\,Ca{=}Ho_2 + \mathbf{H{-}H}. \qquad [183]$$

The metal is obtained with difficulty, either by the electrolysis of the melted chloride, or by decomposing the iodide with sodium.

189. **Calcic Carbonate.** $Ca{=}O_2{=}C\,O$. — The chief lime mineral. Remarkable for the great variety of its crystalline forms. Dimorphous (hexagonal and orthorhombic). The hexagonal forms (Figs. 34, 36, 37, 60, 61, and 62) belong to the mineral species Calcite. The orthorhombic forms (§ 108) to the species Aragonite. *Sp. Gr.* of Calcite, 2.72; of Aragonite, 2.94. The last is also distinguished from the first by superior hardness, and by falling to powder when heated. The crystalline varieties of calcite are readily recognized by a very striking rhombohedral cleavage. Limestones, Oolite, Chalk, Marble, Travertine, Tufa, Calcareous Marl, are names of varieties of rocks, which consist chiefly or wholly of one or the other of these two minerals, generally of calcite. Many of these rocks make excellent building stones. All the varieties of calcic carbonate dissolve with effervescence in dilute nitric and other acids, and may thus be distinguished from the silicious minerals which they sometimes outwardly resemble. Calcic carbonate, although nearly insoluble in pure water, is readily dissolved by water charged with $C\,O_2$. Thus it is held in solution by the water of lime districts, and to a greater or less extent by most spring water. Such water, when strongly charged, deposits calcic carbonate on exposure to the air, and thus are formed stalactites, tufa, and travertine. It also forms deposits in boilers, and decomposes the soap used in washing. (Hard water.) Calcic carbonate may be readily formed artificially by the reaction

$$(CaCl_2 + (NH_4)_2{=}C\,O_3 + Aq) = \mathbf{Ca{=}CO_3} + (2(NH_4)Cl + Aq). \qquad [184]$$

Singularly, however, if the products of the reaction are boiled together, the reverse change takes place; ammonic carbonate, being a volatile substance, is formed, and escapes with the steam, while calcic chloride remains in the solution.

190. **Calcic Oxide (Quick-lime).** CaO. — Obtained by burning limestone in kilns.

$$Ca{=}CO_3 = CaO + \textcircled{C}\textcircled{O}_2. \qquad [185]$$

Amorphous white solid. Very infusible, and emitting an intense white light when ignited (Drummond Light). Has strong affinity for water, and the chemical union is attended with the evolution of much heat (slaking). Exposed to the air, it gradually absorbs both water and carbonic anhydride (air slaking).

191. **Calcic Hydrate.** $Ca{=}Ho_2$. — A light dry powder. Soluble in about 425 parts of cold water (lime-water). With a smaller quantity of water it forms a sort of emulsion called milk of lime, and with still less water it gives a somewhat plastic paste, which, mixed with sand, is ordinary mortar. Hydraulic cements, which harden under water, are made from limestones containing from fifteen to thirty-five per cent of finely divided silica or clay; also by intimately mixing with chalk a due proportion of clay under regulated conditions, and subsequently burning. Calcic hydrate acts on the skin like a caustic alkali, and is used by the tanners for removing hair from hides. It has a strong affinity for CO_2, and hence is used for rendering soda and potash caustic [100]. It is also employed for purifying coal-gas, and in many other processes of the arts. It is largely used as a manure. White-wash is milk of lime mixed with a little glue.

192. **Chloride of Lime or Bleaching Powder,** $CaOCl_2$, is formed by passing chlorine gas into leaden chambers containing slaked lime, which absorbs the gas very rapidly.

$$CaO + Cl{-}Cl = (Ca{-}O){=}Cl_2. \qquad [186]$$

Very much used in the arts for bleaching cotton goods. The cloth having been well washed and digested in a weak solution of chloride of lime, is passed into very dilute sulphuric acid, which liberates the chlorine in the fibre of the cloth. May be used in the laboratory as a source of chlorine gas.

$$(CaOCl_2 + H_2SO_4 + Aq) = (CaSO_4 + H_2O + Aq) + \textcircled{Cl}{-}\textcircled{Cl}. \qquad [187]$$

May also be used as a source of oxygen.

$$2\,CaOCl_2 \underset{\text{Heated.}}{=} 2\,CaCl_2 + O_2.$$

Corresponding to $(Ca{=}O){=}Cl_2$ we have $(Ca{=}O){=}O$, calcic peroxide, formed by adding H_2O_2 to lime-water, but it is a very unstable compound.

193. **Calcic Sulphate.** $Ca{=}O_2{=}SO_2$. — Second in importance of the lime minerals. It occurs in nature both in an anhydrous and a hydrous form. The anhydrous mineral is called Anhydrite, the hydrous mineral is Gypsum. Anhydrite crystallizes in the orthorhombic system (§ 108), and has *Sp. Gr.* 2.9. Gypsum ($CaSO_4 . 2\,H_2O$) crystallizes in the monoclinic system (Fig. 45), has *Sp. Gr.* 2.3, and is softer than the anhydrite. Calcic sulphate is soluble in about 400 parts of water, and, like several of the lime salts, is much less soluble in hot water than in cold; and when water holding gypsum in solution is heated to a high temperature in steam-boilers, the whole is deposited in an insoluble condition ($CaSO_4 . \frac{1}{2}\,H_2O$). It is a very common impurity of spring waters, and is another cause of their hardness, and of the crust which they sometimes form on the inner surface of boilers. It is found in considerable quantity in the water of salt springs, and of the ocean. When these waters are evaporated, it is deposited before the common salt. Hence in nature we find that beds of rock-salt are usually associated with anhydrite and gypsum. The last is by far the most abundant mineral, forming in some places extensive rock deposits of great thickness. It is, moreover, found in beautifully transparent crystals (Selenite), which can be easily split into very thin plates, and it also forms the ornamental stone called alabaster. When heated, gypsum readily gives up its water of crystallization, and when not overburnt the dry product, if reduced to powder and made into a paste, again unites with water and sets into a hard mass. This reunion, however, will not take place if the gypsum has been heated above 300°; and anhydrite is then formed. The calcined gypsum, called Plaster of Paris, is used in immense quantities for making casts, and in various forms of stucco-work. Ground gypsum is also used for dressing land, and finds other applications in the arts.

194. **Calcic Phosphate.** $Ca_3O_6(PO)_2$. — The chief earthy constituent of the bones of animals. The animal obtains it from plants, and the plant draws its supply from the soil. The grains of the cereals are especially rich in this bone-making material, and as the

supply in the soil is usually limited, these plants, when cultivated year after year, soon exhaust it. Hence it is all important for the agriculturist to restore to his land the phosphates as fast as they are removed by the crops, and ground bones, guano, phosphorite, and other forms of calcic phosphate, are used for this purpose. The mineral Apatite is a crystalline variety (Fig. 34) of this same material, but contains also about eight per cent of calcic fluoride mixed with more or less calcic chloride. Its symbol may be written $(Ca_2F)_{10}O_{9}{}_{10}(PO)_2$.

195. **Calcic Silicate (Tabular Spar)**, $CaO_2{\cdot}SiO_2$, is a not uncommon mineral. Formed on the surface of the grains of sand when mortar hardens, and the valuable qualities of hydraulic cements are probably due to a still more complete union of the same kind. An artificial stone of great strength may be made by first mixing together solutions of calcic chloride and sodic silicate, and then incorporating with the half-fluid mass a large proportion of sand.

196. **Calcic Fluoride (Fluor-Spar)**. CaF_2. — An abundant mineral, and the most important compound of fluorine. It is found both massive and crystallized in the forms of the isometric system, generally in cubes. Has octahedral cleavage. The pure material is colorless, but the native crystals are frequently beautifully colored, and are among the most splendid specimens of our mineral cabinets. Exposed to the light, they frequently exhibit a remarkable fluorescence, and many varieties of the mineral phosphoresce when heated. Although not very fusible by itself, fluor-spar forms a very fusible slag with gypsum and other earthy minerals frequently associated with lead ores. This property renders it a valuable *flux* in the process of smelting such ores, and hence the name Fluor. In small quantities it is almost invariably associated with calcic phosphate, not only in the mineral kingdom, but also in the bones and teeth of animals.

197. **Calcic Chloride**. $CaCl_2$. — A deliquescent salt, readily obtained by dissolving calcic carbonate in hydrochloric acid. Also a secondary product in the preparation of ammonia.

$$CaCO_3 + (2\,HCl + Aq) = (CaCl_2 + H_2O + Aq) + CO_2. \quad [188]$$

A useful reagent, and also employed, on account of its hygroscopic qualities, for drying gases.

198. **Calcic Nitrate**. $(CaO_2{\cdot}(NO_2)_2$. — Also a very soluble deliquescent salt, which is formed in the soil, in cellars, in lime caverns, and wherever organic matter decays in contact with calcareous materials. Chiefly important as a source of saltpetre.

199. **STRONTIUM**, $Sr = 87.6$, and **BARIUM**, $Ba = 137.1$.—Bivalent. The compounds of these elements are closely allied to the corresponding compounds of calcium, and the differences are only those which we should expect between members of the same chemical series. They are, however, far less abundantly distributed in nature. The most important native compounds are

Strontic Carbonate,	Strontianite,	$SrCO_3$,	*Sp. Gr.* 3.70.
Baric Carbonate,	Witherite,	$BaCO_3$,	*Sp. Gr.* 4.32.

These are isomorphous with Aragonite. No hexagonal forms corresponding to Calcite are known. In like manner we have

Strontic Sulphate,	Celestine,	$SrSO_4$,	*Sp. Gr.* 3.95.
Baric Sulphate,	Heavy Spar,	$BaSO_4$,	*Sp. Gr.* 4.48.

These are isomorphous with anhydrite. No hydrous minerals corresponding to gypsum are known. Strontic sulphate is much less soluble in water than calcic sulphate, and baric sulphate is practically insoluble. Moreover, the solubility of these salts is not increased by the presence of weak acids. Hence a solution of calcic sulphate will give a precipitate in solutions containing either strontium or barium, and a solution of strontic sulphate only in the last. The sulphates are both easily prepared artificially from solutions of corresponding chlorides by precipitation with sulphuric acid.

200. The **Strontic and Baric Nitrates** and the **Strontic and Baric Chlorides** are all soluble salts, but less soluble than the corresponding salts of calcium, the barium compounds being in each case the less soluble of the two. They are easily prepared by dissolving the native carbonates in dilute nitric or hydrochloric acids. Baric nitrate is precipitated from its aqueous solution by strong nitric or hydrochloric acid, in consequence of its sparing solubility in these reagents. They may also be prepared from the native sulphates, as is illustrated by the following reactions:—

$$SrSO_4 + 4C = SrS + 4\,\mathbb{CO}.$$
$$(SrS + 2\,HCl + Aq) = (SrCl_2 + Aq) + \mathbb{H_2S}. \qquad [189]$$

An intimate mixture of the powdered sulphate with some carbonaceous material is first intensely heated in a crucible. The resulting

product is then exhausted with water, and the solution treated with hydrochloric or nitric acid as required.

201. **Strontic and Baric Hydrates** may also be prepared from the solution of the sulphides, obtained as above, by the reaction

$$CuO + (BaS + H_2O + Aq) = CuS + (Ba^{=}H_{o_2} + Aq). \quad [190]$$

The relative solubility of the hydrates follows the inverse order of that of the other salts, baric hydrate being much the most soluble and dissolving in twenty parts of water.

202. **Strontic and Baric Oxides** may be readily obtained by igniting the nitrates. They slake when mixed with water, like quicklime.

203. **Strontic and Baric Peroxides** are prepared by heating the oxides in an atmosphere of oxygen gas. They are more stable than calcic peroxide, and baric peroxide is an important reagent.

204. **Characteristic Reactions.** — Calcium, strontium, and barium are all precipitated from their solutions by alkaline carbonates and by oxalic acid. They may be distinguished from each other by the relative solubility of their sulphates,* and by the colors of their flames, which show characteristic bands with the spectroscope. The compounds of strontium impart to a colorless flame a brilliant crimson color, and those of barium a yellowish green. Hence they are much used by makers of fireworks. The soluble salts of barium are important reagents in the laboratory, and both the native and the artificial sulphates furnish an important white paint.

205. **LEAD.** $Pb = 206.9$. — Bivalent. One of the more abundant metallic elements, found chiefly in mineral veins. The principal ore is Galena, PbS. There is also a native plumbic carbonate called Cerusite ($PbCO_3$, *Sp. Gr.* 6.48), isomorphous with Aragonite, and a native plumbic sulphate called Anglesite ($PbSO_4$, *Sp. Gr.* 6.30), isomorphous with Anhydrite.

206. **Metallic Lead.** Pb ? — *Sp. Gr.* 11.36. Melting-point, 325°. So soft that it can be moulded by pressure. Obtained, —

1st. By alternately roasting and melting the galena in a reverberatory furnace.

* Calcic sulphate gives an instantaneous precipitate in solutions of barium salts, while in those of strontium the precipitate only forms after a perceptible interval of time.

Roasting stage,

$$3\,PbS + 3\,O_2 = PbS + 2\,PbO + 2\,SO_2,$$

or

$$2\,PbS + 2\,O_2 = PbS + PbSO_4; \qquad [191]$$

Melting stage,

$$PbS + 2\,PbO = 3\,Pb + SO_2,$$

or

$$PbS + PbSO_4 = 2\,Pb + 2\,SO_2. \qquad [192]$$

2d. By smelting the galena with scrap-iron in a blast-furnace,

$$PbS + Fe = FeS + Pb. \qquad [193]$$

Practically, however, both processes are far more complex than the reactions would indicate. The ore is in all cases mixed with gangue, which can only be melted with the aid of some flux, and the slags thus formed contain a large amount of metal, and must be smelted again.

Lead dissolves readily in *dilute* nitric acid, but is not acted on, or only very slightly, by either hydrochloric or sulphuric acids, unless concentrated and boiling. Employed in numberless ways in the arts, both pure and alloyed with other metals. Type-metal, britannia-metal, and solder are among the most important of its alloys.

207. **Plumbic Oxide.** PbO. — Obtained by heating lead in a current of air, when, if the heat is not too great, a yellow powder is obtained called massicot. At a heat a little below redness the oxide melts, and crystallizes on cooling in yellowish red scales called litharge. Largely used in the arts for making flint-glass, for glazing earthenware, and for preparing various paints and lead salts.

208. **Plumbic Peroxide.** PbO_2. — A dark brown powder, very useful in the laboratory as an oxidizing agent. The bright red powder called minium, obtained by still further roasting massicot at a low heat, is a mixture of PbO_2 and PbO. There is also a suboxide, Pb_2O.

209. **Plumbic Hydrate.** — The normal hydrate, $Pb(HO)_2$, has never been obtained, but we can readily form

Diplumbic Hydrate,	$(Pb\text{-}O\text{-}Pb)(HO)_2$,
Triplumbic Hydrate,	$(Pb\text{-}O\text{-}Pb\text{-}O\text{-}Pb)(HO)_2$,

by the following reactions:—

$$2\,Pb(NO_3)_2 + (4\,K\text{-}HO + Aq) = (Pb\text{-}O\text{-}Pb)(HO)_2 + (4\,K\text{-}NO_3 + H_2O + Aq). \qquad [194]$$

$$((Pb_3O_2)\text{-}(C_2H_3O_2)_2 + 2\,(NH_4)\text{-}Ho + Aq) = (Pb_3O_2)\text{-}Ho_2 + (2\,(NH_4)\text{-}(C_2H_3O_2) + Aq). \quad [195]$$

A plumbic hydrate is formed by the simultaneous action of air and water on lead, which is slightly soluble; and as all lead salts are poisonous, and even in minute quantities (if the dose is often repeated) may be injurious to health, it is unsafe to use, for drinking, water which has been kept in lead-lined cisterns, or, in case of some waters, which has been drawn through lead pipes. The presence of nitrites, nitrates, or chlorides greatly increases the corrosive action of water on lead, while carbonates and sulphates exert a preservative influence.

210. **Plumbic Nitrate.** $(Pb\text{-}(NO_3)_2$. — Obtained by dissolving litharge or lead in dilute nitric acid. Soluble in water, but insoluble in strong nitric acid.

$$PbO + (2\,H\text{-}NO_3 + Aq) = (Pb\text{-}(NO_3)_2 + H_2O + Aq). \quad [196]$$

$$3\,Pb + (8\,H\text{-}NO_3 + Aq) = (3\,Pb\text{-}(NO_3)_2 + 4\,H_2O + Aq) + 2\,NO. \quad [197]$$

211. **Plumbic Acetate (Sugar of Lead).** $Pb\text{-}(C_2H_3O_2)_2 . 3\,H_2O$. — The most important soluble salt of lead, easily obtained by dissolving PbO in acetic acid. Lead has a great tendency to form basic salts (§ 39). Hence a solution of the neutral acetate will dissolve a large additional quantity of litharge.

$$2\,PbO + (Pb\text{-}(C_2H_3O_2)_2 + Aq) = ((Pb\text{-}O\text{-}Pb\text{-}O\text{-}Pb)\text{-}(C_2H_3O_2)_2 + Aq). \quad [198]$$

If CO_2 is now passed through this solution, the excess of PbO is precipitated as carbonate. Fresh portions of PbO may then be dissolved and the process repeated. The plumbic carbonate, which is obtained by this and other analogous methods, is very much used as a white paint under the name of white lead. The products of the different processes have not, however, the same composition, but are mixtures of the carbonate and hydrate in varying proportions.

212. **Plumbic Sulphate,** $PbSO_4$, is obtained as a white precipitate on adding sulphuric acid or a soluble sulphate to a solution of a salt of lead. It is practically insoluble in pure water and *dilute* sulphuric acid. It dissolves, however, to a limited extent in *strong* sulphuric acid, and is therefore present in the oil of vitriol of commerce, which is concentrated in lead pans. Hence the white precipitate when the acid is diluted with water.

213. **Plumbic Phosphate** is found in nature in the mineral Pyromorphite, which is isomorphous with Apatite, and has an analogous constitution $(Pb_5Cl)^{IX}O_9^{IX}(PO)_3$. The mineral Mimetine is the corresponding isomorphous arseniate. A melted globule of plumbic phosphate assumes on cooling a peculiar radiated crystalline structure, which is very characteristic.

214. **Plumbic Chloride,** $PbCl_2$, may be obtained as a white crystalline powder by the reactions

$$PbO + (2\,HCl + Aq) = PbCl_2 + (H_2O + Aq). \quad [199]$$

$$(Pb(NO_3)_2 + 2\,HCl + Aq) = PbCl_2 + (2\,HNO_3 + Aq). \quad [200]$$

It is only very slightly soluble in cold water, but in boiling water dissolves quite readily.

215. **Plumbates.** — Caustic alkalies dissolve PbO very freely, forming salts in which the lead plays the part of a negative radical. Hence the precipitate formed in reaction [194] dissolves in an excess of the reagent, and a solution of PbO in lime-water is used as a hair-dye.

216. **Characteristic Reactions.** — The lead compounds, in many of their reactions, are closely allied to the compounds of the first three elements of this group. For example, the soluble salts give precipitates with the alkaline carbonates and with oxalic acid. But in other reactions there are marked differences. Thus, — 1. A strip of metallic zinc placed in a solution of plumbic acetate precipitates all the lead.

$$Zn + (Pb''(C_2H_3O_2)_2 + Aq) = Pb + (Zn''(C_2H_3O_2)_2 + Aq). \quad [201]$$

2. Sulphuretted hydrogen gas passed through either an acid or an alkaline solution of a salt of lead gives a black precipitate of plumbic sulphide.

$$(Pb''Cl_2 + H_2S + Aq) = PbS + (2\,HCl + Aq). \quad [202]$$

When the solution is acidified with hydrochloric acid, the precipitate is at first red, owing to the formation of $(Pb\text{-}S\text{-}Pb)''Cl_2$; but this is soon converted into the black sulphide. 3. Heated on charcoal before the blowpipe, with reducing fluxes, the compounds of lead yield a soft, malleable bead of metal, and the charcoal immediately around the bead is at the same time coated with an incrustation of oxide, which is orange-colored while hot, but becomes lemon-yellow when cold. By these reactions lead is easily distinguished from calcium, strontium,

and barium. Indeed, the distinction is so marked, that, although the resemblances are very striking, it may be doubted whether lead belongs to the same chemical series.

REACTIONS AND PROBLEMS.

1. Calcite and Aragonite are both not unfrequently found in acicular crystals. How may they be distinguished?

2. Compare the molecular volumes of Calcite and Aragonite.

3. By igniting 100 parts of pure calcic carbonate, Dumas obtained exactly 56 parts of lime. What is the atomic weight of calcium? Ans. 40.

4. What assumptions are made in the last problem? (§ 20.)

5. How much CaO can be obtained from 100 kilogrammes of pure limestone? How much $Ca=Ho_2$ will this amount yield?

Ans. 56 kilo. and 74 kilo.

6. How much limestone must be burnt to yield 560 kilo. of quicklime? How many cubic metres of CO_2 would be set free in the process?

Ans. 1,000 kilo. and 223.1 m^3

7. In one cubic metre of limestone assumed to be pure calcic carbonate, *Sp. Gr.* 2.72, how many cubic metres of CO_2 are condensed? Ans. 607.1 m^3

8. What is the cause of the incrustation of boilers by calcic carbonate?

9. Lime-water is used to purify certain hard waters. Explain the reaction.

10. A bed of limestone, *Sp. Gr.* 2.75, 100 metres thick, would make a bed of anthracite coal of what thickness? Assume that the *Sp. Gr.* of anthracite is 1.8, and that it contains 90 per cent of carbon.

Ans. 20.37 metres.

11. In order to precipitate lime as completely as possible with ammonic carbonate, it is important to avoid an excess of ammonium salts, and to warm the liquid, but not to boil it. Give the reasons for these precautions. Also analyze reactions [184 and the reverse], and state the principle under which they may be brought.

12. One cubic decimetre of quick-lime, *Sp. Gr.* 3.18, will absorb how many cubic decimetres of water? How many units of heat will be evolved by the change of state which the water undergoes? Ans. 1.022 $d.m^3$

13. In burning quick-lime it is found that the process succeeds best in damp weather, and is facilitated by injecting steam into the kiln. Why should you infer that this would be the case? (§ 63.)

14. Give an explanation of the hardening and adhesion of mortars and cements.

15. When milk of lime is spread over walls in the process of whitewashing, what compound is formed on the surface?

16. How many cubic metres of CO_2 can be absorbed by a quantity of milk of lime, containing 112 kilo. of lime (CaO)?

17. When lime-water is shaken up with CO_2 it is rendered turbid. How do you explain the reaction, and to what application of lime-water in the laboratory does it point?

18. In order to render 100 kilo. of sal soda caustic, how much quick-lime must be used? [100.] Ans. 52.83 kilo.

19. How many litres of chlorine gas would be absorbed by 100 kilo. of lime (CaO) first changed to hydrate, and how much MnO_2 must be used to yield the requisite amount? Ans. in part, 39.85 litres of chlorine.

20. Bleaching salts have been regarded as a mixture of calcic chloride with calcic hypochlorite. How would you write the symbol on this theory?

21. Represent by graphic symbols $CaCO_3$, CaO_2, $CaOCl_2$.

22. The percentage composition of Gypsum is calcium, 23.26; sulphur, 18.61; oxygen, 37.21; water, 20.92. Calculate the symbol.

23. Is the incrustation of steam-boilers by insoluble calcic sulphate due to the same cause as the incrustation of salt-pans by Gypsum? Explain the difference.

24. If the calcium contained in one cubic decimetre of Anhydrite could be replaced by H_2, what would be the volume of the product formed?

25. If a concentrated solution of sodic sulphate is mixed with a concentrated solution of calcic chloride, the whole mass becomes solid. Write the reaction, and explain what becomes of the water of solution.

Ans. $(Na_2SO_4 + CaCl_2 + 2\,H_2O) = 2\,NaCl + CaSO_4 \,.\, 2\,H_2O$.

26. How could you detect the presence of sulphuric acid and lime in a solution of Gypsum? Write the reactions.

27. Represent the constitution of Apatite by a graphic symbol.

28. How may you regard Apatite as derived from calcic hydrate? What important part does fluorine play in the compound? Does not the presence of such a univalent element in this compound furnish an argument in favor of the bivalence of calcium?

29. How much hydrochloric acid, *Sp. Gr.* 1.1, will be required to dissolve 50 grammes of chalk, and how many litres of CO_2 could be thus obtained? Ans. 179 grammes of acid, and 11.16 litres of CO_2.

30. By what single reaction could you change a solution of calcic nitrate into a solution of nitre?

31. Compare the molecular volumes of the native carbonates of strontium, barium, and lead, with those of Aragonite and Calcite.

32. Write the reactions by which strontic and baric sulphates may be prepared from the corresponding nitrates or chlorides.

33. Analyze the reactions by which the chlorides and nitrates of strontium and barium may be prepared from the corresponding sulphates, and show why such a circuitous method is necessary.

34. Compare the molecular volume of the sulphates of this group with that of the corresponding carbonates.

35. How may solutions of calcic and strontic sulphates be used to detect barium and strontium, even if mixed together in the same solution?

36. Knowing that sulphuric acid if in excess will completely precipitate barium and strontium, how can you detect the presence of lime in a solution containing all three?

37. On what does the use of the salts of barium as tests for sulphuric acid depend?

38. To how much SO_3 does 0.932 gramme of baric sulphate correspond?
Ans. 0.320 gramme.

39. A quantity of Witherite weighing 0.591 gramme was dissolved in hydrochloric acid and precipitated with sulphuric acid. The precipitate when washed, dried, and ignited weighed 0.699 gramme. What per cent of barium does the mineral contain? Ans. 69.37 per cent.

40. Baric and strontic carbonates are not, like calcic carbonates, easily decomposed when heated in the air, but readily give off CO_2 if heated in an atmosphere of hydrogen. How do you explain these facts? and do they confirm or otherwise your answer to question 13?

41. What is the percentage of lead in the three minerals Anglesite, Cerusite, and Galena? Ans. 68.32 %, 77.54 %, 86.61 %.

42. Analyze reactions [191–193] and state the general theory of the smelting process, including the removal of the gangue and the reduction of the ore.

43. Explain the peculiar action of lead with acid solvents. Why must the nitric acid be diluted, and to what extent?

44. How many kilo. of litharge can be obtained from 37.1 kilo. of lead, and what volume of oxygen gas would be absorbed in the process?
Ans. 39.96 kilo. and 2 m³

45. Represent the plumbic oxides and hydrates by graphic symbols, and show how the condensed hydrates are related to the assumed normal hydrate.

46. The action of nitric acid on lead depends on the degree of concentration and on the temperature. Write the reaction assuming that N_2O is formed; also assuming that NO is formed.

47. How many kilo. of crystallized sugar of lead can be made from 6.69 kilo. of litharge? Ans. 11.37 kilo.

48. How much litharge will a solution containing 11.37 kilo. of sugar of lead dissolve, assuming that triplumbic acetate is the product formed?
Ans. 13.17 kilo. PbO.

49. Write the reaction of CO_2 on a solution of basic acetate of lead.

50. How may the basic acetates be regarded as derived from the normal hydrates?

51. Write the reaction of dilute sulphuric acid on a solution of plumbic nitrate.

52. Represent the constitution of Pyromorphite and Mimetine by graphic symbols.

53. What is the derivation of the name Pyromorphite?

54. Will the whole of the lead be precipitated from its solution in acetic acid by an excess of $HCl + Aq$?

55. By what reagent may you precipitate the whole of the lead from a solution of one of its salts?

56. Why should a solution of PbO in lime-water blacken the hair, or any other organic material containing sulphur?

57. How could you detect the presence of lead in water?

58. From a solution containing all the members of this group, how could you separate the whole of the lead?

59. The solubility of the compounds of the elements of this group diminishes, as a general rule, in proportion as the atomic weight of the metallic radical increases. Does this fact conform to the law which generally obtains in chemical series in regard to the chemical energy of the different members?

DIVISION X.

217. **MAGNESIUM.** $Mg = 24$. — Bivalent. One of the most widely distributed elements, although not so abundant as Calcium, with which it is usually associated. In some of its relations it is very closely allied to calcium, but also differs from it in many important respects.

218. **Metallic Magnesium,** Mg, is readily obtained by decomposing the anhydrous chloride with metallic sodium, and also by electrolysis. It is a silver-white metal, melting at a red heat, and volatilizing at a high temperature in an atmosphere of hydrogen. It is malleable and ductile, is susceptible of a high polish, and does not tarnish in dry air. Heated in the air it takes fire and burns with great splendor [56], and it is now much used as a source of pure white light when great brilliancy is required. Boiling water acts upon the metal quite rapidly, but cold water is decomposed only very slowly.

219. **Magnesic Oxide (Calcined Magnesia),** MgO, is obtained when the metal is burnt in air. It can also be obtained by calcining the carbonate or the nitrate. It is a bulky white powder, wholly infusible, and emitting a bright white light when heated before the blowpipe. Intensely heated, it appears to volatilize unchanged. When mixed with water it slowly unites with it to form a hydrate. The oxide obtained by calcining the nitrate is much denser than that made from the carbonate, and possesses remarkable hydraulic qualities. When mixed with water it soon sets, forming a hard compact mass resembling marble. If the oxide is heated to a very high temperature, it loses its power of uniting with water, and dissolves only slowly even in the strongest acids. Crystallized MgO (Figs. 25 to 27), Periclase, has been found in small grains imbedded in a limestone rock ejected from Vesuvius, but otherwise it does not occur uncombined in nature.

220. **Magnesic Hydrate,** $Mg{\cdot}O_2{\cdot}H_2$, is found native, crystallized in large hexagonal plates (§ 107), Brucite. It can be readily formed artificially as above; also by adding caustic potash, soda, or baryta to the solution of any of its salts. It is but very slightly soluble in water, yet sufficiently to give a distinct alkaline reaction (§ 46). It absorbs CO_2 slowly from the air, but much more slowly than calcic hydrate.

221. **Magnesic Carbonate.** $Mg''O_2''CO$. *Sp. Gr.* 3.056. — The mineral Magnesite, isomorphous with Calcite. Insoluble in pure water, but in carbonic acid water more soluble than calcic carbonate. This solution is much used as a medicine (liquid magnesia). If exposed to the air, the magnesic carbonate slowly separates in crystalline flakes, containing three molecules of water. Anhydrous magnesic carbonate is not readily obtained artificially. The precipitate obtained on adding sodic carbonate to a boiling solution of a magnesic salt is a mixture of magnesic carbonate and magnesic hydrate in variable proportions (Magnesia Alba). The product, however, appears to be a mixture of several definite compounds of these two salts; and a crystalline mineral is known, called Hydromagnesite, which has the formula $H_4Mg_4O_{12}C_3 . 2H_2O$, or

$$H_{o_4}^{\equiv}(\overset{IV}{C}''O_2''Mg''O_2''C''O_2''Mg''O_2''C) . 2H_2O.$$

Magnesic carbonate is found united with calcic carbonate in the mineral Dolomite (*Sp. Gr.* 2.9). This is by far the most abundant native compound of magnesium, and forms in many localities extensive beds of rocks. It occurs in large and well-defined crystals, which are isomorphous with calcite and magnesite (Fig. 36). The mineral is somewhat variable in its composition, and may either be regarded as an isomorphous mixture of these two substances, or else as a definite compound mixed with an excess of one or the other of its constituents.

$$MgCO_3 + CaCO_3, \quad \text{or} \quad (MgO_2)''(C''O_2''C)''(CaO_2).$$

When calcined at not too high a temperature, the magnesic carbonate is alone decomposed, and a product obtained which forms an excellent hydraulic cement. From the calcined mass the magnesia can be dissolved out by carbonic acid water and freed from the lime. In this way pure magnesic carbonate is prepared.

222. **Magnesic Sulphate (Epsom Salt).** $MgSO_4 . 7H_2O$. — The most important soluble salt of magnesium. Obtained from the bittern of sea-water, or by treating the native carbonates or Dolomite with sulphuric acid. It is a very common ingredient of mineral waters, like those of Epsom, and is formed when water saturated with gypsum filters through Dolomitic rocks. The salt, with seven molecules of water, is dimorphous, crystallizing both in orthorhombic forms isomorphous with $ZnSO_4 . 7HO$, and in monoclinic forms isomor-

phous with $FeSO_4 . 7HO$. It may also be obtained crystallized with 1, 2, 3, ... 12 molecules of water under regulated conditions, chiefly of temperature. The compound $MgSO_4 . H_2O$ (Kieserite) is found in the Stassfurt salt-beds. Epsom salt is reduced to the same composition when heated to 150°, but the last molecule of water is retained even at 200°, and this leads us to believe that it forms a part of the molecule of the salt, whose formula would then be written $MgO_2{=}SO{=}H_2$. This opinion is confirmed by finding that this molecule of water may be replaced by the molecule of an alkaline sulphate, forming a double salt, which crystallizes with $6\,H_2O$ in the same form as magnesic sulphate with $7\,H_2O$. The symbol of the potash salt is

$$(MgO_2){=}(SO{=}O_2{=}OS){=}(KO)_2 . 6\,H_2O.$$

Epsom salt dissolves in about three times its weight of cold water. It is a valuable medicine, but, like all the soluble salts of magnesium, it has a bitter, disgusting taste.

223. **Magnesic Silicates.** — The well-known minerals, Serpentine, Talc (Soapstone), and Chrysolite (Olivine), are essentially magnesic silicates; and in many other native silicates, including the Hornblendes, Augites, Chlorites, and some varieties of Mica, magnesium is one of the principal basic radicals.

224. **Magnesic Chloride.** $MgCl_2$. — Found dissolved in sea-water, and the cause of its bitter taste. Obtained by dissolving magnesic carbonate in hydrochloric acid, and evaporating in an atmosphere of hydrochloric acid gas. If evaporated in the air, the salt is partially decomposed. Very fusible. Used for making magnesium. Forms double salts with alkaline chlorides (§ 155).

225. **Characteristic Reactions.** — Magnesium, although closely related to calcium, is distinguished from the alkaline earths by the great solubility of its sulphate, also by its tendency to form soluble double salts with ammonium, in consequence of which no precipitate is formed in solutions of its salts either by ammonia or ammonic carbonate, when sufficient excess of some ammonium salt is present. The ammonio-magnesic phosphate, however, $(NH_4){,}Mg{=}O_3{=}PO . 6\,H_2O$, is insoluble, and is formed whenever sodic phosphate is added to an ammoniacal solution of a magnesium salt. This reaction furnishes the most delicate test for magnesium salts.

226. **ZINC.** $Zn = 65.2$. — Bivalent. One of the more abundant metallic elements. The principal ores are

Red Oxide of Zinc,*	ZnO	Hexagonal,
Blende,	ZnS	Isometric,
Smithsonite,	$(ZnO_2)''CO$	Hexagonal,
Calamine,	$(ZnO_2)_2''Si \cdot 2H_2O$	Trimetric.

The ores are reduced by first roasting or calcining until the metal is in the condition of an oxide, and then distilling with a mixture of coal in earthen retorts or muffles.

227. **Metallic Zinc.** Zn. — *Sp. Gr.* 6.8 to 7.2. Fuses at 500°. Boils at a red heat. The polished surface has a bright lustre, with a bluish tint, but soon tarnishes in moist air. Has a crystalline structure, but, although brittle both at a high and a low temperature, it may readily be rolled out into sheets at a temperature of about 140°. Sheet-zinc is nearly as cheap as sheet-iron ; and since it does not rust, or at most only very superficially, it is preferable for many purposes. Iron, however, is a much stronger metal, and is frequently coated with zinc to protect it from rusting. It is then said to be galvanized. Zinc readily dissolves in dilute acids with the evolution of hydrogen, and is much used in the laboratory, together with dilute sulphuric acid, for making this gas. The metal is first granulated by pouring it, when melted, into water. When boiled with a solution of caustic soda or potash, it also dissolves with evolution of hydrogen.

$$Zn + (2\,KO\text{-}H + Aq) = (K_2O_2''Zn + Aq) + H\text{-}H. \quad [203]$$

It is used as the electro-positive metal in the galvanic battery.

228. **Zincic Oxide,** ZnO, which is made in large quantities by burning zinc vapor at the mouth of the reduction furnaces, is a very light white powder, much used, when mixed with oil, as a white paint. A denser oxide is obtained by calcining zincic nitrate.

229. **Zincic Hydrate,** $Zn''Ho_2$, is formed by the reaction

$$(ZnSO_4 + 2\,K\text{-}Ho + Aq) = Zn''Ho_2 + (K_2SO_4 + Aq), \quad [204]$$

but is soluble in an excess of reagent.

230. **Zincic Carbonate,** $ZnCO_3$, is isomorphous with Magnesite and Calcite. When prepared by precipitation, a mixture of hydrate and carbonate is formed, as in § 221.

231. **Zincic Sulphate (White Vitriol).** $ZnSO_4 \cdot 7H_2O$. — Very soluble salt, isomorphous with Epsom salt, which it closely resembles

* The color is due to the presence of a small amount of manganese.

in most of its chemical relations, forming similar double salts. Preparation as in [64]. Used in pharmacy.

232. **Zincic Chloride.** $ZnCl_2$. — A solution of zinc in hydrochloric acid can be concentrated by evaporation without decomposition. All the water is not driven off until the temperature reaches 250°. The result is a thick syrup, which forms, on cooling, a white, deliquescent solid, melting at 100°, called by the alchemists Butter of Zinc. It has an intense affinity for water, and by its aid the elements of water may frequently be removed from a chemical compound without producing any further change. Thus, alcohol may be converted by it into ether or ethylene. According to the proportions used, we have

$$C_2H_6O - H_2O = \underset{\text{Ethylene.}}{C_2H_4}, \quad \text{or} \quad 2C_2H_6O - H_2O = \underset{\text{Ether.}}{2C_2H_6O}. \quad [205]$$

For the same reason it acts as a cautery on the skin. It is also used in solution as an antiseptic and disinfecting agent.

233. **Zinc and the Alcohol Radicals.** — Zinc Methide, $Zn(CH_3)_2$; Zinc Ethide, $Zn(C_2H_5)_2$; Zinc Amylide, $Zn(C_5H_{11})_2$. Observed Sp. Gr. of vapor, 3.29, 4.26, and 6.95 respectively. Obtained both by heating zinc with the iodides of methyl, ethyl, or amyl in sealed tubes, and by the action of zinc on the mercury compounds of the same radicals. They are all three colorless, transparent, strongly refracting, and mobile liquids. They are also volatile, boiling at the temperatures of 46°, 118°, and 220° respectively. They are likewise highly inflammable, and the first two take fire spontaneously in the air. As these compounds do not, as a whole, combine with any of the elements, their molecules are evidently saturated, and they are interesting as fixing beyond all doubt the atomic relations of zinc. Moreover, they are useful reagents in many processes of organic chemistry.

234. **Characteristic Reactions.** — Zinc, like magnesium, forms soluble double salts with ammonia, but it is easily distinguished by the fact that its sulphide is insoluble, not only in solutions of the fixed alkalies, but also in those of ammonia and the ammonium salts. Hence it is precipitated from all alkaline solutions by sulphuretted hydrogen. The sulphide thus obtained is a white precipitate, soluble in dilute mineral acids, but insoluble in acetic acid.

235. **Cadmium.** $Cd = 112$. — *Sp. Gr.* 8.69. Bivalent. A comparatively rare element associated with zinc. As metallic cadmium is more volatile than its associate, it accumulates in the dust which collects in the early stages of the process of distilling zinc from its

ores. Cadmium resembles zinc in forming similar oxides and hydrates and similar soluble salts. But, on the other hand, it differs from zinc in many important respects. It is less soluble in acids, its hydrate is insoluble in caustic alkalies, its basic carbonate is insoluble in excess of ammonic carbonate, and its yellow sulphide is insoluble in cold dilute mineral acids in presence of H_2S. This sulphide is found in nature, and the mineral is called Greenockite. The sulphide obtained by precipitating a solution of a salt of cadmium with H_2S is much used as a yellow paint. The great stability of this sulphide is one of the most characteristic features of cadmium. Cadmic sulphate, if heated in an atmosphere of H_2S, is readily reduced to the sulphide, and this reaction has been used for determining the atomic weight of the element. Zinc precipitates cadmium from solutions of its salts. Cadmium melts at 242°, and an alloy of cadmium with lead, tin, and bismuth melts at 60°. Cadmium boils at 860°, and the Sp. Gr. of its vapor has been observed to be 56.85.

QUESTIONS AND PROBLEMS.

1. Write the reaction of sodium on magnesic chloride.

2. When water is decomposed by magnesium, what are the products? Write the reaction. [39.]

3. How do you account for the intense brilliancy of the light emitted by burning magnesium? (§ 81.)

4. Write the reaction of water on calcined magnesia. [41.]

5. Write the reaction of a solution of caustic soda on a solution of magnesic chloride. Ans. $(MgCl_2 + 2\,NaHo + Aq) = MgHo_2 + (2\,NaCl + Aq)$.

6. Represent the composition of Hydromagnesite by graphic symbols.

7. Represent graphically the compound radicals MgO_2, CaO_2, ZnO_2, and show their relations to hydroxyl.

8. Represent graphically the composition of Dolomite.

9. What do you understand by the term isomorphous mixture?

10. Explain the theory of the preparation of magnesic carbonate from Dolomite.

11. The symbol of magnesic sulphate may be written either $MgSO_4$, or $Mg{=}O_2{=}SO_2$, or $MgO_2{=}SO_2$. What different relations do these forms suggest?

12. Write the reaction of sulphuric acid on the two constituents of Dolomite, and show that pure Epsom salt may be thus prepared.

13. Write the reaction of a solution of Gypsum on magnesic carbonate.

14. Represent by graphic symbols $MgSO_4 . H_2O$.

15. Represent by graphic symbols the composition of potassio-magnesic sulphate, and explain the relations of the crystallized salt to Epsom salt.

16. Write the reaction of hydrochloric acid on magnesic carbonate.

17. Explain the decomposition which results when a solution of magnesic chloride is evaporated in the air, and why an atmosphere of HCl should prevent the change.

18. What is the difference between the relations of baric and magnesic carbonate to calcic carbonate?

Ans. The first is related to Aragonite, the second to Calcite.

19. What is the difference between the reactions of sodic carbonate on solutions of calcic and magnesic salts, and on what does the difference depend? Write the reactions in the two cases.

20. What is the difference between the reaction of ammonic carbonate on the same solutions?

21. Write the reaction of sodic phosphate on an ammoniacal solution of magnesic chloride.

Ans. $(MgCl_2 + NH_3 + H, Na_2{=}O_2{=}PO + Aq) =$
$(NH_4), Mg{=}O_2{=}PO . 6\,H_2O + (2\,NaCl + Aq)$

22. Write the reactions when zinc blende and Smithsonite are calcined.

Ans. $ZnCO_3 = ZnO + CO_2$, and $2\,ZnS + 3\,O_2 = 2\,ZnO + 2\,SO_2$.

23. Write the reaction when zincic oxide is reduced.

Ans. $ZnO + C = Zn + CO$

24. Write the reactions of dilute sulphuric, hydrochloric, and acetic acids on zinc.

25. What part does zinc play in reaction [203]?

26. In what different ways may the symbol of zincic hydrate be written?

Ans. $Zn{=}O_2{=}H_2$, $Zn{=}Ho_2$, ZnO_2H_2.

27. When zincic hydrate dissolves in caustic soda, what is formed?

28. Write the reaction of sodic carbonate upon a solution of zincic sulphate, assuming that three molecules of zincic hydrate are formed to every two molecules of zincic carbonate.

Ans. $(5\,ZnSO_4 + 5\,Na_2CO_3 + 3\,H_2O + Aq) =$
$2\,\mathbf{ZnCO_3} + 3\,\mathbf{ZnHo_2} + (5\,Na_2SO_4 + Aq) + 3\,\mathbf{CO_2}$.

29. In what different ways may the symbol of zincic sulphate be written, both the anhydrous salt and the salt with one molecule of water? Represent graphically.

30. Write the symbol of potassio-zincic sulphate. What is the crystalline form of this double salt, and with how many molecules of water does it crystallize?

31. Write the reaction of ammonic sulphide on a solution of zincic sulphate. Ans. $(ZnSO_4 + (NH_4)_2S + Aq) = \mathbf{ZnS} + ((NH_4)_2SO_4 + Aq)$.

32. Write the reaction of sulphuretted hydrogen on a solution of zincic acetate.

33. Would zincic sulphide be precipitated from a solution of zincic chloride containing an excess of hydrochloric acid? What is the difference between this case and that of problem 32? (§ 22).

Cadmium.

34. Write the reaction of dilute sulphuric acid on cadmium.

35. Write the reaction of sodic hydrate on a solution of cadmic sulphate.

36. Write the reaction of sulphuretted hydrogen on a solution of cadmic chloride.

37. By what reagents may cadmium be separated from zinc?

Ans. By metallic zinc, by ammonic carbonate, and by sulphuretted hydrogen.

38. Show how the atomic weight of cadmium may be determined by reducing $CdSO_4$ to CdS. To what known atomic weights is the atomic weight of cadmium then referred, and to what extent would any error in these values influence the result.

39. Assuming that the atomic weight of cadmium is 112, what inference may be drawn from the Sp. Gr. of its vapor in regard to the constitution of its molecule? Does the conclusion have any bearing on the molecular constitution of other bivalent elements?

DIVISION XI.

236. **NORWEGIUM.** $Ng = 145.9$, if the oxide is NgO. — This name has been given to a metal obtained from a sample of copper-nickel of Kragerö, Norway. The color of the metal is said to be white, with a slight brownish cast. When polished it has a perfectly metallic lustre, but after a time it becomes covered with a thin film of oxide. It can be flattened out in an agate mortar, and in hardness resembles copper. The melting point is 350°, and the *Sp. Gr.* 9.441. Only one oxide has been obtained. With H_2S it gives a brown sulphide, even in strongly acid hydrochloric acid solutions, which redissolves in ammonic sulphide. With potassic ferrocyanide it gives at first a brown, but with larger proportions a green precipitate. It dissolves in dilute sulphuric acid, and is precipitated from this solution by metallic zinc in a pulverulent state. The solutions of the metal are blue, but become green on dilution. We copy the description as it has been given, but this does not give us the means of classifying the element, and we place it here provisionally.

DIVISION XII.

237. **COPPER.** $Cu = 63$. — Bivalent. One of the most abundant metals, and known from great antiquity. Of its ores, by far the most important is Copper Pyrites, Fe_2S_2Cu, which is found to a greater or less extent in almost all countries. This mineral resembles iron pyrites, but is distinguished from it by greater softness and a ruddier tint. The smelting of the ore is a complex process, and consists in an alternating series of roastings and meltings, during which the iron passes into the slags, while the copper accumulates in the successive "mattes," as they are called, until at last a nearly pure sub-sulphide is obtained. This is now heated in a current of air until the metal is partially oxidized, and then the mass is melted, when the following reaction results: —

$$2\,CuO + Cu_2S = 4\,Cu + SO_2. \qquad [206]$$

The crude metal thus obtained must, however, be subsequently refined. To this end it is first kept melted in the air for many hours, until all

the impurities are oxidized; and then the oxides of copper, formed at the same time, are reduced by submitting the mass to the action of carbonaceous gases, which are generated by thrusting a stick of green wood under the molten metal.

238. **Metallic Copper.** *Cu.* — Found native crystallized in forms of the isometric system. Has a brilliant lustre, and a familiar reddish color. Has great hardness and tenacity. Is very ductile and malleable, and one of the best conductors of heat and electricity. Sp. Gr. 8.8. Fuses at about 780°. Volatilizes only at a very high temperature. Its vapor burns with a beautiful green flame, which shows in the spectroscope characteristic bands. Under ordinary conditions copper undergoes no change in the atmosphere, but if heated to redness in the air it is rapidly oxidized. In presence of acids or solutions of chlorides, like sea-water, copper absorbs oxygen from the air at the ordinary temperature, and is more or less rapidly corroded. A similar effect is also produced by aqua ammonia and solutions of ammonium salts. Out of contact with the air, dilute hydrochloric or sulphuric acids have but little action upon metallic copper. If boiled with strong hydrochloric acid in a state of fine division (cement copper), it very slowly dissolves with the evolution of hydrogen gas and the production of Cu_2Cl_2. Under the same conditions sulphuric acid, if not too dilute, is decomposed by it, cupric sulphate is formed, sulphurous oxide is evolved, and the reaction is similar to [151]. Nitric acid is the best solvent, but, singularly, the strongest acid has no action on the metal. When diluted with water, however, the action is very violent; cupric nitrate is formed, and a gas is evolved which is generally NO; but when the acid is very dilute this product is more or less mixed with N_2O.

239. **Cupric Oxides.** $[Cu_2]O$ and CuO. — Both of these act as basic anhydrides, but the second yields by far the most stable and important compounds. $[Cu_2]O$ has a red color, and when melted into glass imparts to it a beautiful ruby or purple color. It is the Red Oxide of Copper of mineralogy, and is found massive and beautifully crystallized in various forms of the isometric system, also in splendid capillary tufts (Chalcotrichite). CuO is black, but imparts to glass a green color. It is found sparingly in nature, rarely crystallized (Black Oxide of Copper, or Melaconite). May be prepared by roasting copper or by igniting the nitrate. Is very easily reduced by hydrogen [67], or by carbonaceous materials, and is much used as an

oxidizing agent in the process of organic analysis. The following reactions illustrate some of the relations of these oxides and their hydrates:—

When cold, $(Cu{=}O_2{=}SO_2 + 2\,K{-}O{-}H + Aq) =$

$$Cu{=}O_2{=}H_2 + (K_2{=}O_2{=}SO_2 + Aq). \quad [207]$$

By boiling, $(\underset{\text{Blue.}}{Cu{=}O_2{=}H_2} + Aq) = \underset{\text{Black.}}{CuO} + (H_2O + Aq).$ [208]

By boiling with grape sugar,

$(2\,Cu{=}O_2{=}SO_2 + 4\,K{-}O{-}H - O + Aq) =$

$$\underset{\text{Red.}}{[Cu_2]O} + (2\,K_2{=}O_2{=}SO_2 + 2\,H_2O + Aq). \quad [209]$$

An orange-yellow hydrate, $4\,[Cu_2]O\,.\,H_2O$, is precipitated on first warming the liquid, but this is rendered anhydrous by boiling.

240. **Cupric Sulphate (Blue Vitriol).** $Cu{=}O_2{=}SO_2\,.\,5\,H_2O$.—The most important soluble salt of copper. Although when pure it always crystallizes with five molecules of water, as above, yet it is capable of forming isomorphous mixtures with ferrous sulphate, $Fe{=}O_2{=}SO_2\,.\,7\,H_2O$. When in this mixture the copper is in excess, the crystals take $5\,H_2O$ and the form of cupric sulphate (Fig. 48). If, however, the iron is in excess, they take $7\,H_2O$ and the form of ferrous sulphate similar to Fig. 46. The anhydrous salt is white, but becomes blue on uniting with water, for which it has a very strong affinity. Of the five molecules of water with which the crystalline salt is united, one is held much more firmly than the other four, and may be replaced by a molecule of an alkaline sulphate. This gives a reason for writing the symbol of the salt thus: $Ho_2, Cu\,O_2{=}SO\,.\,4\,H_2O$. In like manner the symbols of several so-called basic salts may be written thus:—

$$H_{2}, (Cu\,O_2H)_2{=}SO,$$
$$Ho_2, (CuO_2H)_4{=}S \text{ (Brochantite)},$$
$$Ho, (CuO_2H)_5{=}S\,.\,2\,H_2O,$$

in which the group $Cu\,O_2H$ may be regarded as a monad radical. From solutions of cupric sulphate the copper is readily precipitated by *Zn* or *Fe*.

$$Zn + (CuSO_4 + Aq) = Cu + (ZnSO_4 + Aq). \quad [210]$$

241. **Carbonates.** — Malachite, $(Cu\,O_2H)_2{=}C\,O$. Same compound may be obtained by mixing hot solutions of cupric sulphate and sodic carbonate. Azurite, $(Cu\,O_2)_2, Ho_2$ or $Ho, Cu\,O_2{=}C{-}Cu\,O_2{-}C{=}Cu\,O_2, Ho$

Mysorin, $(CuO_2)_2^{\equiv}C$. Neither the normal carbonate $CuO_2{=}CO$, nor the ortho carbonate $(CuO_2)_2^{\equiv}C$, is known.

242. **Nitrates.** — $CuO_2{=}(NO_2)_2 \,.\, 6\,H_2O$ when crystallized below 60°, and $CuO_2{=}(NO_2)_2 \,.\, 3\,H_2O$ when crystallized above 60°, a deliquescent blue salt. A green basic nitrate has the symbol

$$Ho_3,(CuO_2H)_3,CuO_2{}^{\text{viii}}N_2O.$$

243. **Cupric Phosphate,** $(CuO_2)_3^{\equiv}(PO)_2$, is obtained on adding a solution of sodic phosphate to a solution of cupric sulphate.

244. **Cupric Silicate.** Dioptase, $Ho,(CuO_2H){=}SiO$.

245. **Sulphides :** —

Copper Glance,	$[Cu_2]S$
Covelline (Indigo Copper),	CuS
Copper Pyrites,	$Fe{=}S_2{=}Cu$
Erubescite,	$Fe{=}S_2{=}([Cu_2]{-}S{-}[Cu_2])$
Tetrahedrite,	$[Cu_2]_3^{\equiv}S_6^{\equiv}Sb_2 \,.\, ZnS$

When H_2S is passed through the solution of a copper salt, a black precipitate falls having the composition $Cu_6S_6Ho_2$, which rapidly oxidizes in the air.

246. **Fluohydrate of Copper.** $Cu{=}Ho,F$.

247. **Chlorides.** — Cuprous Chloride, $[Cu_2]Cl_2$. White compound, insoluble in water, crystallizes in tetrahedrons. Cupric Chloride, $CuCl_2 \,.\, 2\,H_2O$, crystallizes in green needles, very soluble in both water and alcohol. Cupric Oxichloride, $(Cu_4O_3){=}Cl_2 \,.\, 4\,H_2O$, is much used as a paint (Brunswick green), and the mineral Atacamite is the same compound, with only one, or at most two, molecules of H_2O.

248. **Cupric Hydride.** CuH_2. — A brown powder, which gives, with hydrochloric acid, the following remarkable reaction : —

$$CuH_2 + (2\,HCl + Aq) = (CuCl_2 + Aq) + 2\,H{-}H. \qquad [211]$$

249. **Ammoniated Compounds.** — When a solution of ammonia or of ammonic carbonate is added to a solution of a salt of copper, the light green precipitate first produced readily dissolves in an excess of the reagent, producing a deep blue solution ; and this striking coloration is one of the most characteristic tests of the presence of copper. The effects are caused by the formation of certain remarkable compounds, in which a portion of the hydrogen of the ammonia appears to have been replaced by copper. The following are a few examples : —

$(H_2,H_2,H_2\overset{\text{III}}{N}_2[Cu_2])Cl_2$, $(H_2,H_2,(NH_4)_2\overset{\text{III}}{N}_2[Cu_2])I_2$,

$(H_2,H_2,H_2\overset{\text{III}}{N}_2Cu)Cl_2$, $(H_2,H_2,(NH_4)_2\overset{\text{III}}{N}_2Cu)SO_4 . H_2O$.

250. **Characteristic Reactions and Uses.** — The presence of copper in a solution may be readily detected, not only by ammonia as indicated above, but also by the action of polished iron (a needle, for example), which, in a feebly acid solution, soon becomes covered with a red metallic coating. Copper ores, when mixed with fluxes, are readily reduced on charcoal before the blowpipe, and this is one of the best means of recognizing such compounds.

Besides the numerous uses of the metal itself, copper is employed in the arts still more extensively when alloyed with other metals. The varieties of brass and yellow metal are alloys of copper and zinc in different proportions, while bronze, bell-metal, gun-metal, and speculum-metal are all essentially alloys of copper and tin. Several of the compounds of copper are much used as paints.

251. **MERCURY.** $Hg = 200$. — Bivalent. This element is not widely disseminated, but its ores are abundant in a few localities, of which the most noted are Idria in Austria, Almaden in Spain, New Almaden in California, and Huancavelica in Peru. The ores at all these localities consist chiefly of Cinnabar, HgS, but they frequently contain a small quantity of the metal in the native state. They are easily smelted, the sulphur of the ore serving as fuel. The assorted ores are arranged in layers in kilns of peculiar construction, and the mass kindled with brushwood. As the sulphur burns away, the mercury is volatilized, and the products thus formed are passed through earthen pipes ("aludels") or brick chambers, which condense the mercury vapor, while the SO_2 gas escapes into the atmosphere.

$$HgS + O_2 = Hg + SO_2. \qquad [211]$$

In the Palatinate, mercury is obtained from cinnabar by mixing the ore with lime and distilling in iron retorts.

$$4\,HgS + 4\,CaO = 3\,CaS + CaSO_4 + Hg. \qquad [213]$$

252. **Metallic Mercury.** Hg. — The only metal liquid at ordinary temperatures. Freezes at $-40°$. Boils at $350°$ and evaporates, but only with exceeding slowness at the ordinary temperature. Sp. Gr. of liquid, 13.596. Sp. Gr. of vapor by experiment, 100.7. Has a brilliant metallic lustre, silver-white color. In solid condition is mal-

able, crystallizes in octahedrons, *Sp. Gr.* 14.4. In contact with the air pure mercury undergoes no change at the ordinary temperature, but if boiled in the atmosphere it is slowly converted into HgO. Hydrochloric acid is without action on the metal, and the same is true of dilute sulphuric acid. Strong sulphuric acid, however, is decomposed by it [151]. The best solvent is nitric acid, which yields different products according to the proportions of metal, acid, and water used. Chlorine, bromine, iodine, and sulphur all enter into direct union with mercury. By simple trituration the liquid metal admits of being mechanically mixed in a state of minute subdivision with chalk, and with saccharine or oleaginous substances, and many important pharmaceutical preparations are made in this way, — blue-pills, mercurial ointments, etc.

253. **Oxides of Mercury.** — Mercurous Oxide, $[Hg_2]O$. Black powder, very unstable. Decomposed by exposure to light or to a very gentle heat. $[Hg_2]O = HgO + Hg$. Mercuric oxide, HgO. Red crystalline scales or yellow powder, according to mode of preparation. Stable compound, but decomposed at red heat into mercury and oxygen [114]. No corresponding hydrates are known, but both oxides form stable salts.

254. **Nitrates.** — Mercurous nitrate is obtained by dissolving metallic mercury in an excess of nitric acid diluted with four or five times its bulk of water. Mercuric nitrate is best obtained by dissolving mercuric oxide in an excess of nitric acid. These, like other salts of mercury, tend to form basic compounds.

Mercurous Nitrate, $[Hg_2]{=}O_2{=}N_2O_4 . 2\,H_2O$

Dimercurous Nitrate, $([Hg_2]{-}O{-}[Hg_2]){=}O_2{=}N_2O_4$

Trimercurous Dinitrate, $([Hg_2]{-}O{-}[Hg_2]{-}O{-}[Hg_2]){=}O_2{=}(N_2O_4{-}O{-}N_2O_4) . 3\,H_2O$

Mercuric Nitrate, $Hg{=}O_2{=}N_2O_4 . 2\,H_2O$

Dimercuric Nitrate, $(Hg{-}O{-}Hg){=}O_2{=}N_2O_4 . 2\,H_2O$

Trimercuric Nitrate, $(Hg{-}O{-}Hg{-}O{-}Hg){=}O_2{=}N_2O_4 . H_2O$

A solution of mercurous nitrate with caustic soda gives a black precipitate of mercurous oxide.

$$([Hg_2]{=}O_2{=}N_2O_4 + 2\,Na{-}O{-}H + Aq) = [Hg_2]O + (2\,Na{-}O{-}NO_2 + H_2O + Aq). \quad [214]$$

A solution of mercuric nitrate with caustic soda gives a yellow precipitate of mercuric oxide.

$$(Hg''O_2''N_2O_4 + 2\,Na'O'H + Aq) = HgO + (2\,Na'O'NO_2 + H_2O + Aq). \quad [215]$$

Mercurous nitrate, if heated, is converted into the red crystalline variety of mercuric oxide.

$$[Hg_2]''O_2''N_2O_4 = 2\,HgO + 2\,NO_2. \quad [216]$$

255. **Sulphates.** — When mercury is gently heated with an excess of strong sulphuric acid, Mercurous Sulphate, $[Hg_2]''O''SO_2$, is formed; but if the heat be increased, and the evaporation carried to dryness, the first product is changed into Mercuric Sulphate, $Hg''O_2''SO_2$, which is a white crystalline powder, readily dissolving in a solution of common salt, but decomposed by pure water into a soluble acid and an insoluble basic salt. The last is known as Turpeth-Mineral. It has a yellow color, and its composition is expressed by the symbol,

$$(Hg'O'Hg'O'Hg)''O_2''SO_2.$$

Mercurous sulphate is also prepared for the manufacture of calomel by triturating together mercuric sulphate with a quantity of mercury equal to that which it already contains.

256. **Sulphides.** — Mercurous Sulphide, $[Hg_2]S$, obtained as a black precipitate on passing H_2S gas through the solution of a mercurous salt. Very unstable, like the corresponding oxide. Mercuric Sulphide (Vermilion, Cinnabar), HgS, is precipitated by the same reagent from the solution of a mercuric salt. But when the reagent is not in excess, and especially if the solution is concentrated, the precipitate contains chlorosulphide of mercury in varying proportions, and has accordingly different shades of color, from white through reddish brown to black. The pure precipitated HgS is black, but when sublimed the substance acquires the peculiar vermilion tint. Vermilion is usually prepared by rubbing together mercury and sulphur, and subliming the black product. Crystals are frequently thus obtained identical in form with those of natural cinnabar (§ 107).

257. **Chlorides.** — Mercurous Chloride (Calomel), $[Hg_2]Cl_2$, may be obtained either as a white powder or in crystals (§ 106), —

1st. By subliming a mixture of mercuric chloride and mercury,

$$HgCl_2 + Hg = [Hg_2]Cl_2. \quad [217]$$

2d. By subliming a mixture of mercurous sulphate and common salt,

$$[Hg_2]SO_4 + 2\,NaCl = Na_2SO_4 + [Hg_2]Cl_2. \qquad [218]$$

3d. By precipitation from a solution of mercurous nitrate,

$$([Hg_2]N_2O_6 + 2\,NaCl + Aq) = [Hg_2]Cl_2 + (2\,NaNO_3 + Aq). \qquad [219]$$

Calomel is insoluble in water, alcohol, and ether. The Sp. Gr. of its vapor is only one half of that which the theory would require, — an anomaly which is explained as an effect of dissociation. Sublimes below a red heat without melting. When triturated with a solution of soda or potash, it is turned black, owing to the formation of $[Hg_2]O$, and when heated with alkaline chlorides it is converted into $HgCl_2$. In the presence of organic matter, acids, and air, this last change may take place, to some extent at least, at a temperature of 38° or 40°. Calomel is an invaluable medicine. It was first prepared by rubbing together in a mortar $Hg + HgCl_2$, but this product, although having all the medicinal properties of the white sublimate, had a brilliant black color, whence the name, from καλὸς μέλας.

258. **Mercuric Chloride (Corrosive Sublimate).** $HgCl_2$. — Crystalline (§ 108) white solid, melting at 265°, boiling at 293°, and yielding a vapor whose Sp. Gr. (141.5) conforms very nearly to the theory. Soluble in water, alcohol, and ether. Forms salts with the alkaline chlorides, as $2\,NaCl.\,HgCl_2$. May be prepared by subliming a mixture of mercuric sulphate and common salt, but adding a small amount of MnO_2 to the mixture to prevent the formation of calomel. Also formed when mercury is burnt in chlorine gas. Acts as a violent poison. Coagulates albumen, and forms with it, as well as with other albuminoid substances, stable compounds insoluble in water. Used for preserving wood, dried plants, and other objects of natural history from decay, and this effect appears to be due in part to its peculiar action on albuminoid compounds. It is also a valuable reagent, and is used to prepare other anhydrous chlorides.

Mercury forms, like copper, a large number of oxichlorides. It also combines with the other members of the chlorine group of elements. Among these compounds the most interesting is the iodide, HgI_2, which affects two different crystalline forms distinguished also by striking differences of color. As obtained by precipitation,

$$(HgCl_2 + 2\,KI + Aq) = HgI_2 + (2\,KCl + Aq), \qquad [220]$$

it appears as a crystalline red powder (§ 106). This when heated changes its crystalline condition (§ 108) and becomes yellow, but the yellow variety is changed back to the red by mere friction.

259. **Ammoniated Compounds.** — The compounds of mercury, when acted on by ammonia or by ammonium salts, yield a large number of complex products. Among these the most remarkable is a powerful base called Mercuramine, which is formed by the action of aqua ammonia upon yellow precipitated oxide of mercury. There is a difference of opinion in regard to the arrangement of the atoms in this compound, but the most probable symbol is

$$(\overset{II}{Hg},(Hg\overset{I}{O}H),H\equiv N)\text{-}O\text{-}H\,.\,H_2O.$$

The hydrate absorbs CO_2 from the air, and forms definite salts with all the common acids. This compound is unstable; but when heated, two molecules of the hydrate give up three molecules of water, and there is left a dark brown product permanent in the air, whose symbol may be represented after the type $[H_4N]_2O$. The following are the symbols of a few only of the many mercurial compounds of this class: —

$H_2, H_2{\equiv}N_2{-}[Hg_2]$	Formed by the action of ammonia gas on precipitated calomel.
$H_2, [Hg_2]{\equiv}N_2{-}[Hg_2]$	Black compound, formed from calomel by action of aqua ammonia.
$(H_2, H_2, Hg{\equiv}N_2{-}Hg)Cl_2$	"White Precipitate," formed by adding to aqua ammonia a solution of $HgCl_2$.
$(H_2, H_2, H_2{\equiv}N_2{-}Hg){-}Cl_2$	"Soluble White Precipitate."

260. **Characteristic Reactions and Uses.** — The salts of mercury, whether soluble or insoluble, are all reduced to the metallic state by a solution of stannous chloride. Any of the salts heated in a closed tube with sodic carbonate give a sublimate of minute globules of mercury. From solutions of its salts mercury is deposited as a gray film on metallic copper, and if short lengths of copper wire thus coated and carefully dried be heated in a closed tube, the sublimate is obtained as before.

The chief consumption of metallic mercury is in the treatment of gold ores. It is also used for silvering mirrors, for making various philosophical instruments, and for other purposes in the arts. Large quantities are consumed in preparing its various compounds, and these are among the most important articles of the materia medica.

QUESTIONS AND PROBLEMS.

1. Write the reaction of boiling sulphuric acid on copper.

2. Write the reaction of nitric acid on copper, — 1st, assuming that NO is the aeriform product; 2d, that it is N_2O.

3. Write the reaction which takes place when cupric nitrate is decomposed by heat.

4. Why does not concentrated nitric acid act on copper?

5. Represent the constitution of the hydrate $4[Cu_2]O \cdot H_2O$. How may it be regarded as related to the normal hydrate $[Cu_2]{=}Ho_2$?

Ans. It equals $4[Cu_2]{=}Ho_2 - 3\,H_2O$.

6. How may anhydrous cupric sulphate be used to detect the presence of moisture?

7. In what other way may the symbols of the different basic sulphates be written?

Ans. The symbol of Brochantite may be written $(Cu\text{-}O\text{-}Cu\text{-}O\text{-}Cu\text{-}O\text{-}Cu){=}O_2{=}SO_2 \cdot 3\,H_2O$, and the others in a similar way.

8. How may the symbols of the basic sulphates be derived from the hydrates?

Ans. Disregarding the water of crystallization, we may regard Brochantite as formed from the condensed hydrate $4\,Cu{=}O_2{=}H_2$ by first eliminating $3\,H_2O$ and then replacing the remaining H_2 by SO_2.

9. If the symbol of Brochantite is written as in the text, to what order of sulphates does it belong? Ans. Orthosulphates.

10. Show by graphic symbols that the radical CuO_2H must be univalent.

11. Represent by graphic symbols the composition of Malachite and Azurite.

12. Both Malachite and Azurite may be regarded as formed by the molecular union of cupric hydrate and cupric carbonate. Write the symbols on this theory.

13. Malachite is how related to cupric hydrate?

Ans. It may be regarded as the hydrate doubly condensed with two of the hydrogen atoms replaced by CO thus: $Cu_2{\equiv}O_4{\equiv}CO,H_2$, or $Cu{=}O_2{=}CO \cdot Cu{=}O_2{=}H_2$. Symbol of Azurite in the same way becomes $Cu_3{\equiv}O_6{\equiv}(CO)_2,H_2$, or $2\,Cu{=}O_2{=}CO \cdot Cu{=}O_2{=}H_2$.

14. To what order of carbonates does Mysorin belong?

15. In what other ways may the symbol of the cupric nitrates be written?
Ans. $Cu{=}O_2{=}(NO_2)_2$ and $Cu_2{\equiv}O_4{\equiv}NO_2H_2$, or $Cu{=}O_2{=}(NO_2),H.Cu{=}O_2{=}H_2$.

16. Write the symbol of Dioptase in the same typical form.
Ans. $H_2Cu{=}O_2{\equiv}Si$.

17. To what order of silicates may Dioptase be referred?
Ans. Orthosilicates.

18. Write the reaction of a solution of sodic phosphate on a solution of cupric sulphate.

19. Represent the constitution of the various sulphides of copper by graphic symbols.

20. In what relation does the fluohydrate of copper stand to the hydrate and fluoride of the same metal?
Ans. It holds an intermediate position, as shown by the symbols $Cu{=}H_2$, $Cu{=}Ho,F$, and CuF_2.

21. Regarding the molecule of water in the common variety of Atacamite as water of constitution, how may the formula of this mineral be simplified?
Ans. It may be halved and written $(Cu\text{-}O\text{-}Cu){=}Ho_2Cl$.

22. How is Atacamite related to cupric hydrate?
Ans. $2\,Cu{=}Ho_2 = (Cu\text{-}O\text{-}Cu){=}Ho_2 + H_2O$, then replacing one atom of H in the condensed hydrate by Cl.

23. What do you find that is remarkable in the reaction of cupric hydrate on hydrochloric acid? Compare it with reaction [121], and consider whether it indicates a difference of condition in hydrogen similar to that in oxygen.

24. Write the symbols of the ammonio-compounds of copper in a graphic form.

25. What evidence can you find that a portion of the nitrogen atoms in two of the compounds stand in a different relation to the molecule from the others?
Ans. If the nitrogen atoms were all alike, we should expect the basic radicals to fix more than the equivalent of two univalent acid radicals.

26. Write the symbols of the hydrates which correspond to the different basic nitrates of mercury, and show how such condensed hydrates may be derived from the assumed normal hydrates.

27. How is it possible that salts should exist corresponding to hydrates that cannot be isolated?

28. Show how turpeth-mineral may be derived from an assumed normal hydrate.

29. How would you seek to determine whether the black product obtained by grinding together $Hg + S$ is a mixture or a compound?

30. By experiment it appears that the specific gravity of calomel vapor is 118.5. What should it be theoretically? Into what is it probably decomposed when heated? Ans. 235.5; Hg and $HgCl_2$.

31. In administering calomel as medicine, what associations with other drugs should be avoided?

32. How may calomel be distinguished from corrosive sublimate?

33. What is the theoretical Sp. Gr. of $HgCl_2$, and why should you anticipate so great a difference between it and the experimental result?

Ans. 135.5. In such a dense vapor the deviation from Mariotte's law would probably be large.

34. Write the reaction which takes place when a mixture of mercuric sulphate and common salt is sublimed.

35. In cases of poisoning by corrosive sublimate, why should milk or the white of eggs be useful as temporary antidotes, until the stomach can be emptied by an emetic or otherwise?

36. Write the symbols of the chloride, nitrate, sulphate, and carbonate of mercuramine.

37. Write the symbol of the oxide of mercuramine described above.

38. Represent by symbols the constitution of the different ammoniated compounds of mercury.

DIVISION XIII.

261. **NICKEL.** $Ni = 58.8$. — Quantivalence usually two. One of the less abundant metallic elements. The chief native compounds are

Breithauptite,	Hexagonal,	$Ni^{II}_2[Sb_2]$
Kupfernickel,	Hexagonal,	$Ni^{II}_2[As_2]$
Chloanthite (Nickeliferous Smaltine),	Isometric,	$Ni^{II}[As_2]$
Nickel Glance,	Isometric,	$Ni^{II}[S_2,[As_2]]$
Rammelsbergite,	Orthorhombic,	$Ni^{II}[As_2]$
Millerite,	Hexagonal,	$Ni=S$
Bunsenite,	Isometric,	$Ni=O$
Nickel Vitriol,	Monoclinic,	$Ni=O_2=SO_2 \cdot 7\,H_2O$
Annabergite (Nickel green),	Monoclinic,	$Ni^{II}_3O^{II}_8(AsO)_2 \cdot 8\,H_2O$
Emerald Nickel (Zaratite),		$Ni^{II}_3O^{II}_6CO,H_4 \cdot 4\,H_2O$
Genthite,		$[Ni,Mg]_4{}^{VIII}O_6{}^{VIII}Si_3O_3 \cdot 6\,H_2O$

The metal is obtained chiefly from a nickeliferous iron pyrites (magnetic variety), which only contains the element as an accessory constituent. The native arsenides, and an impure regulus (called *speiss*) formed in the preparation of smalt, are the other sources of the nickel of commerce. The process of extracting the metal is complicated and tedious. It consists in roasting the ore, dissolving the resulting oxides in acid, and precipitating first the associated metals, and afterwards the nickel, by appropriate reagents. The chief difficulty is to separate from the nickel the more valuable cobalt, with which nickel is almost invariably associated, and to which it is very closely allied.

Metallic nickel, *Sp. Gr.* 8.82, has a silver-white color, a brilliant metallic lustre, and does not tarnish when exposed to the atmosphere. It has great tenacity and malleability, and, were it more abundant, would rival even iron in the number of its applications in the useful arts. Nickel resembles iron in many of its qualities. When pure, it is nearly as infusible as *wrought iron*, and may be forged in a similar way. When combined with a small amount of carbon, it may, like *cast iron*, be fused in an ordinary wind furnace. Nickel is also

like iron, susceptible of magnetism, but the magnetic power is less marked, and, when heated, it loses this virtue at a much lower temperature. Moreover, like iron, nickel is soluble in dilute sulphuric or hydrochloric acids, with evolution of hydrogen gas; but the action is less energetic, and the metal dissolves only slowly. The best solvents are nitric acid and aqua regia. Nickel forms with copper a brilliant white, hard, tenacious, malleable alloy, and a small amount of nickel will whiten a large body of copper. This alloy is much used for coinage, and as the basis of the better kinds of electrotype plate. German silver is an alloy of copper, zinc, and nickel, in about the proportion of 5 : 3 : 2. Nickel may also be alloyed with iron, and is a constant constituent of the metallic meteorites. Nickel readily combines with each of the members of the chlorine group of elements, but only in one proportion, and the compounds thus formed, NiF_2, $NiCl_2$, &c., are all soluble in water.

There are two oxides of nickel. The protoxide, NiO, is an olive-green powder, readily obtained by igniting either the nitrate or the carbonate of the metal. It is a basic anhydride, dissolving readily in the mineral acids, and forming the ordinary nickel salts, in all of which *Ni acts as a bivalent radical.* The sesquioxide, Ni_2O_3, is a black powder, also obtained by igniting the nitrate, but at a lower temperature. It is an unstable compound, and, when heated, is resolved into the lower oxide and oxygen gas. It is not a basic anhydride, and, when heated with the mineral acids, one third of the oxygen is given off as before, and a salt of the ordinary type is the result. In the sesquioxide, Ni is a quadrivalent, but the double atom $[Ni_2]$, or $\equiv(\overset{IV}{Ni}\text{-}\overset{IV}{Ni})\equiv$ (§ 35), *acts as a sexivalent radical.* The tendency to form radicals of this last type, which is only foreshadowed in nickel, becomes a striking character in the elements which follow in our classification.

Of the crystallized soluble salts of nickel, the most common are

Nickelous Chloride,	$NiCl_2 \cdot 9H_2O$
Nickelous Nitrate,	$Ni{=}O_2{=}(NO_2)_2 \cdot 6H_2O$
Nickelous Sulphate,	$Ni,H_2^{\equiv}O_4^{\equiv}SO \cdot 6H_2O$
Dipotassio-nickelous Sulphate,	$Ni,K_2^{\equiv}O_4^{\equiv}(SO_2)_2 \cdot 6H_2O$

The salts of nickel, both when crystallized and when in solution, have a characteristic green color; but, when rendered anhydrous by heat, this color changes to yellow. From their solutions the fixed

alkalies precipitate a hydrate, and the alkaline carbonates a basic carbonate, of nickel, both forming pale green precipitates. The first is probably the definite compound $Ni^{II}O_2^{II}H_2$; but the composition of the second varies with the temperature, strength, and proportions of the solutions employed, and the product is closely analogous to the precipitates, which are obtained under similar conditions from solutions of the salts of magnesium or zinc.

The salts of nickel readily combine both with ammonia and with the ammonium salts. A large number of products may thus be formed, which are easily soluble in water. The following crystalline compounds, which indirectly play an important part in some of the methods of qualitative analysis, will serve as types of two different classes of such compounds:—

$$NiCl_2 . 6\,NH_3, \qquad NH_4Cl . NiCl_2 . 6\,H_2O.$$

From solutions of such ammoniacal compounds, and from other alkaline solutions containing nickel, the metal is precipitated as $[Ni_2]^{III}O_6^{III}H_6$, both by chlorine gas and by the alkaline hypochlorites. The precipitate has an intense black color, and this reaction is one of the most delicate tests for nickel, but does not distinguish it from cobalt. Nickel is also precipitated from alkaline solutions by H_2S or by alkaline sulphides. The black precipitate thus obtained ($NiS . Aq$) contains an indefinite amount of water. It is insoluble in the dilute mineral acids, although in acid solutions of nickel salts H_2S gives no precipitate. Two other sulphides of the element, Ni_2S and NiS_2, have been described.

262. **COBALT.** $Co = 58.8$. — Quantivalence usually two. Associated with nickel in the same ores, but less abundantly distributed. Most of the minerals enumerated in the last section contain cobalt. When, however, this metal preponderates, they are in most cases classed as separate mineral species, and receive distinct names. No cobalt mineral corresponding to Kupfernickel or Breithauptite has been found, but we have

Smaltine,	Isometric,	$Co^{II}[As_2]$
Cobaltine,	Isometric,	$Co^{II}[S_2,[As_2]]$
Linnæite,	Isometric,	Co_3S_4
Glaucodot,	Orthorhombic,	$Co^{II}[S_2,[As_2]]$
Syepoorite,		$Co^{II}S$
Cobalt Vitriol,	Monoclinic,	$Co^{II}O_2^{II}SO_2 . 7\,H_2O$
Erythrite (Cobalt Bloom),	Monoclinic,	$Co_3^{II}O_6^{II}(AsO)_2 . 8\,H_2O$

To these must be added an impure oxide of cobalt (Earthy Cobalt), and a mineral called Remingtonite, which probably corresponds to Emerald Nickel. There is a variety of Linnæite, called Siegenite, which contains a large proportion of nickel; but no purely nickeliferous compound of this type is known.

In all their chemical relations, the two metals here associated resemble each other so closely, that the description of nickel given above applies almost word for word to cobalt, and it is only necessary to indicate further the points of difference.

Metallic cobalt rusts more readily than nickel, but less readily than iron. It is magnetic, and possesses valuable qualities, but is so costly that it has received no application in the arts.

Cobalt forms but one stable compound with any one of the members of the chlorine group of elements, $CoCl_2$, &c.; but by dissolving Co_2O_3 in hydrochloric acid a red solution is obtained, which is supposed to contain Co_2Cl_6. The compound, however, is very unstable, for the solution evolves chlorine on the slightest elevation of temperature.

There are three well-marked oxides of cobalt: Cobaltous Oxide, CoO; Cobaltic Oxide, Co_2O_3; Cobaltous-cobaltic Oxide, Co_3O_4; and, besides these, several others have been distinguished, which are probably either mixtures or molecular aggregates of the first two. Not only is CoO a strong basic anhydride, like NiO, but Co_2O_3 also dissolves in acids, especially in acetic acid, forming salts. We have, therefore, to distinguish between cobaltous and cobaltic salts; but the last are very unstable and little known.

The ordinary cobaltous salts, when crystallized, are red, but are usually lilac-colored when anhydrous, and the pink solutions, which they yield with water, become blue when concentrated. On this change of color depends the virtue of certain sympathetic inks. From solutions of these salts, potassic or sodic hydrate precipitates $Co''O_2''H_2$, which has a delicate rose-color. The pale blue precipitate, which generally falls first, is a basic salt of cobalt; but if warmed with an excess of the reagent, it soon acquires the composition and color of the normal hydrate. If exposed to the air this hydrate absorbs oxygen rapidly, and changes to a dingy green color. The black precipitate obtained by the action of chlorine or the hypochlorites on alkaline solutions containing cobalt is the second anhydride of this hydrate, or $O_2'''[Co_2]''O_2''H_2$. The same compound is formed when chlorine gas is passed through water or a solution of caustic potash holding cobaltous

hydrate in suspension. When the alkali is used, the whole of the hydrate is converted into the cobaltic compound; but with pure water only two thirds as much are obtained. The compound of nickel formed under the same conditions is supposed to be the normal nickelic hydrate.

The tendency to form soluble compounds with ammonia and with the ammonium salts, manifested by nickel, appears again and more prominently in the allied element cobalt. Moreover, there are cobaltic as well as cobaltous compounds of this class, and the last tend to pass into the first by absorbing oxygen when exposed to the air. The number of these compounds is very numerous. They have a very complex constitution, and in many cases at least are probably formed on the ammonia type. We may regard them as compounds of ammonio-cobalt bases, to several of which distinctive names have been given. The following scheme exhibits the relations of the more important compounds:—

Cobaltous Compounds.

$$\overset{II}{Co}R . 4NH_3, \qquad \overset{II}{Co}R . 6NH_3.$$

Cobaltic Compounds.

$[Co_2]\overset{II}{R}_3 . 8NH_3$	Fusco-cobaltic salts.
$[Co_2]\overset{II}{R}_3 . 10NH_3$	Roseo or Purpureo-cobaltic salts.
$[Co_2]\overset{II}{R}_3 . 12NH_3$	Luteo-cobaltic salts.

In the above symbols $\overset{II}{R}$ stands for a bivalent acid radical, like (SO_4), (CO_3), (C_2O_4) or Cl_2, $(NO_3)_2$, &c. Substituting these in the general symbol, we obtain the specific symbols of the various salts of the assumed bases; but in most cases the crystallized salt contains in addition one or more molecules of water, which frequently play an important part in its constitution, and determine marked differences of qualities, as in the following typical compounds:—

Purpureo-cobaltic Chloride,	$[Co_2]Cl_6 . 10NH_3$
Roseo-cobaltic Chloride,	$[Co_2]Cl_6 . 10NH_3 . 2H_2O$
Xantho-cobaltic Chloride,	$[Co_2]Cl_6 . 10NH_3 . N_2O_2 . H_2O$

Cobaltous oxide combines with many of the basic, as well as with the acid anhydrides, yielding in several cases compounds distinguished

by great brilliancy of coloring. The compound with $[Al_2]O_3$ is known as Thénard's blue; that with ZnO, as Rinman's green. Such compounds are formed when the metallic oxides, moistened with a solution of cobaltous nitrate, are heated before the blowpipe, and the production of the color is one of the most characteristic blowpipe reactions.

Cobaltous oxide, when melted into glass or into the glaze of earthenware, imparts to the material an intense blue color, and the brilliancy and the depth of the color render the oxide one of the most valuable vitrifiable pigments, and this is its chief use in the arts. The blue pigment called smalt, used for coloring paper and dressing white calicoes, is a pulverized alkaline glass strongly colored with the oxide.

Cobalt is distinguished by the same reactions as nickel from all other metallic radicals. From nickel it is distinguished, — First, by the blue color which the oxide gives to borax glass. Secondly, by the fact that potassic nitrite precipitates * the cobalt from nitric or acetic acid solutions, while it does not precipitate nickel. Thirdly, by the circumstance that cyanide of cobalt forms, when boiled with a solution of potassic cyanide in contact with the air, a compound corresponding to potassic ferricyanide. The solution of potassic cobalticyanide thus formed is not decomposed by HgO nor by alkaline hypochlorites, while from the solution of the cyanide of nickel and potassium, formed under the same circumstances, all the nickel is precipitated by the same reagents.

$$\mathbf{CoO} + (2\,H\text{-}CN + Aq) = \mathbf{Co''(CN)_2} + (H_2O + Aq). \quad [221]$$

$$4\,\mathbf{Co''(CN)_2} + (12\,K\text{-}CN + 4\,H\text{-}CN + Aq) + \mathbf{O{=}O} = (2\,K_6'''(C_{12}N_{12}Co_2) + 2\,H_2O + Aq). \quad [222]$$

$$\mathbf{NiO} + (4\,K\text{-}CN + H_2O + Aq) = (2\,K\text{-}CN\,.\,Ni''(CN)_2 + 2\,K\text{-}O\text{-}H + Aq). \quad [223]$$

$$\mathbf{HgO} + (2\,K\text{-}CN\,.\,Ni''(CN)_2 + H_2O + Aq) = \mathbf{Ni''O_2''H_2} + (2\,K\text{-}CN\,.\,Hg''(CN)_2 + Aq). \quad [224]$$

* Composition of precipitate according to S. P. Sadtler,

$$K_6[Co_2]\,xii\,O_{12}\,xii(N_2O_2)_6\,.\,xH_2O.$$

QUESTIONS AND PROBLEMS.

1. Represent by graphic symbols the constitution of Kupfernickel and Chloanthite.

2. In the symbol of Nickel Glance, in what relation does the sulphur stand to the arsenic? Could these elements replace each other by single atoms?

3. What is the distinction between Chloanthite and Rammelsbergite? Does the same distinction reappear in the corresponding compound of either of the allied elements?

4. Have any facts been stated which *prove* that nickel is sometimes quadrivalent?

5. Represent by a graphic symbol the constitution of nickelous sulphate.

6. Write the reaction of sulphuric acid, and also of hydrochloric acid, on Ni_2O_3.

7. Point out the analogies between nickel and zinc.

8. The precipitate first formed by ammonia or ammonic carbonate in solutions of the salts of nickel redissolves in an excess of the reagent, and does not form at all when a large amount of ammonic chloride is present. How do you explain these reactions?

9. In the native compounds of cobalt this element is more or less replaced by iron and nickel. Write the symbols of Smaltine and Cobaltine so as to indicate this fact.

10. Represent by graphic symbols the constitution of Linnæite, and also that of Co_2S_3 and CoS_2, the only other sulphides not mentioned in the text.

11. Represent by graphic symbols the constitution of the following oxides and oxysulphides, Co_3O_4, Co_6O_7, Co_2OS.

12. In what respects do the oxides and sulphides of cobalt differ from those of nickel?

13. Write the reaction of chlorine gas on cobaltous hydrate, first, when suspended in water, and, secondly, when suspended in a solution of caustic potash. Write also the corresponding reactions which take place when hydrate of nickel is similarly treated.

14. Represent the composition of the ammonio-cobalt salts by typical symbols.

15. In potassic cobalticyanide what is the quantivalence of cobalt? Do the cobalt atoms change their atomicity in [222]?

16. Analyze reactions [221] to [224], and show that the differences in the relations of cobalt and nickel to the alkaline cyanides depend on differences in the atomic relations of the two elements. What part does the oxygen of the air play in [222]?

17. Potassic cobalticyanide is formed when cobaltous hydrate is boiled with a solution of potassic cyanide, there being free access of air. Write the reaction.

18. Write the reaction when a solution of potassic hypochlorite (*K-O-Cl*) is added to the product of reaction [223].

19. Point out the resemblances and the differences in the chemical relations of cobalt and nickel, and show how far they may be traced to the circumstance that the radical $[Co_2]$ is more stable than the radical $[Ni_2]$.

DIVISION XIV.

263. **MANGANESE.** $Mn = 55$. — Remarkable for its variable quantivalence, two, four, six, and possibly seven or eight. A tolerably abundant element, and widely diffused throughout the mineral kingdom, entering into the composition of a very large number of minerals. The following are the most characteristic or important: —

Pyrolusite,	Orthorhombic,	MnO_2
Braunite,	Tetragonal,	Mn_2O_3 or $(Mn{-}Si)^{\equiv}O_3$
Hausmannite,	Tetragonal,	Mn_3O_4
Psilomelane, Wad,	Massive, Earthy,	Mixtures of different oxides.
Manganite,	Orthorhombic,	$O^{\equiv}[Mn_2]{-}O_2{-}H_2$
Hauerite,	Isometric,	MnS_2
Manganblende,	Isometric,	MnS
Rhodonite,	Triclinic,	$Mn_2{-}O_2{-}SiO$
Tephroite,	Orthorhombic,	$Mn_2^{\equiv}O_4^{\equiv}Si$
Triplite,	Orthorhombic,	$([Fe,Mn]_2{-}F){=}O_3^{\equiv}(PO)^{\equiv}$
Manganese Spar,	Rhombohedral,	$Mn{-}O_2{-}CO$
Mangano-calcite,	Orthorhombic,	$[Ca,Mn]{-}O_2{-}CO$

The elementary substance is a very hard and brittle metal, *Sp. Gr.* 8.013. It has a grayish-white color, is almost infusible, and very slightly magnetic. It oxidizes rapidly in moist air, and decomposes water even at the ordinary temperature. There appear to be two conditions of the metal corresponding to wrought and cast iron; but its properties have not been thoroughly studied. It is obtained with difficulty by reducing the oxide with carbon at a very high temperature, and as yet has found no applications in the arts. Corresponding to the three degrees of quantivalence of manganese are three classes of compounds.

1st. Manganous compounds, in which the quantivalence of the element is two. This class includes all the manganese minerals above enumerated, after Manganblende, and all the common soluble salts of the metal. Among the last the most important are, —

Manganous Chloride,	$MnCl_2$. (2 or 4 H_2O)
Manganous Sulphate,	$Mn{-}O_2{-}SO_2$. (4, 5, or 7 H_2O)
Dipotassio-manganous Sulphate,	$K_2Mn^{\equiv}O_4^{\equiv}[SO_4]_3$. 6 H_2O

There is also a bromide, $MnBr_2 . 2H_2O$. The manganous compounds are distinguished by a delicate pink or red color. From solutions of the manganous salts, potassic or sodic hydrate precipitates a white hydrate, $Mn''O_2''H_2$, which absorbs oxygen rapidly, and becomes brown when exposed to the air (Manganese Brown). In like manner, sodic or potassic carbonate precipitates a white hydro-carbonate, which also becomes brown on drying. Ammonic carbonate also produces the same precipitate, and does not redissolve it when added in excess. Ammonic hydrate, on the other hand, gives no precipitate in solutions containing an excess of ammonic chloride, and redissolves the precipitate which first forms in simple aqueous solutions. Ammonio-manganous salts are thus formed, and two well-crystallized ammonio-manganous chlorides have been described,

$$MnCl_2 . 2NH_4Cl . H_2O, \quad \text{and} \quad MnCl_2 . NH_4Cl . 2H_2O.$$

In the solution of a manganous salt, sodic phosphate and ammonia produce, under regulated conditions, a highly crystalline precipitate having the composition $(NH_4)_2,Mn_2'''O_6''(PO)_2 . 2H_2O$. This precipitate yields on ignition a pyrophosphate of uniform composition, and on this reaction is based a valuable means of determining the amount of manganese in quantitative chemical analysis.

Manganous oxide, MnO, is easily obtained by reducing either of the higher oxides with hydrogen. It is an olive-green powder, which burns if heated in the air, thus forming the "red oxide" Mn_3O_4.

Manganous sulphide is precipitated on adding an alkaline sulphide to the solution of a manganous salt, as a flesh-colored hydrate, $MnS . xH_2O$; but this also in contact with the air rapidly oxidizes and turns brown. It readily dissolves in the dilute mineral acids, and also in acetic acid. The same tendency to form compounds in which manganese presents a higher order of quantivalence, is exhibited by all the soluble manganous salts, and especially by the ammoniacal solutions just mentioned, which, when exposed to the air, rapidly absorb oxygen, become turbid, and deposit a brownish flocculent precipitate of manganic hydrate ($O_2''[Mn_2]''H_2''O_2$?). So, also, when chlorine gas is passed through water holding manganous hydrate or carbonate in suspension, or through a solution of a manganous salt to which an excess of sodic acetate has been added, the manganese is still further oxidized, and the brownish precipitate obtained is chiefly a hydrate of the dioxide $MnO_2 . H_2O$. Bromine also produces a similar result.

2d. *Manganic compounds, in which the quantivalence of the element is four.* Of these we must distinguish two divisions: first, those which have for their radical the single quadrivalent atom of manganese; secondly, those in which two such quadrivalent atoms act as a compound radical with a quantivalence of six. To the first division of the manganic compounds probably belong most of the native oxides. Pyrolusite, MnO_2, has a crystalline form similar to that of Brookite, TiO_2, which is an oxide of the well-marked tetrad element titanium; while Braunite, Mn_2O_3, and Hausmannite, Mn_3O_4, have a form which is nearly isomorphous with Rutile, an allotropic state of the same oxide (Fig. 57), but wholly unlike the forms of Fe_2O_3 (Fig. 64) and Fe_3O_4 (Fig. 53), two typical compounds, to which Braunite and Hausmannite, if containing the sexivalent radical $[Mn_2]$, must be closely allied. Manganite probably contains this radical, as it is isomorphous with the native ferric hydrate, Göthite.

Of the oxides of manganese, the red oxide, Mn_3O_4, is the most stable. The higher oxides, when heated, are all resolved into Mn_3O_4, and the native oxides thus become sources of oxygen gas [118]. When heated with sulphuric acid, they also give off oxygen and yield manganous sulphate [117]. When heated with hydrochloric acid, they liberate chlorine and yield manganous chloride [77]. Hence an important application of the native oxides in the arts. There are reasons for believing that the two atoms of oxygen in MnO_2 stand in different relations to this molecular group, and the chloride of manganese, $MnCl_4$, recently isolated, affords still more conclusive evidence of the quadrivalent relations of this element. This manganic chloride is exceedingly unstable, and when gently heated breaks up into manganous chloride and chlorine gas.

To the second division of the manganic compounds belong manganic hydrate, $O_2{=}[Mn_2]{=}O_2{=}H_2$, and several very unstable compounds which have been formed by dissolving this hydrate in different acids. The sulphate, however, becomes stable when the hexad radical is associated in the salt with potassium. We thus obtain an interesting variety of alum,

$$K_2{,}[Mn_2]^{\text{VIII}}O_8{}^{\text{VIII}}[SO_2]_4 \,.\, 24\,H_2O.$$

3d. The most characteristic compounds of manganese are those in which the element is either sextivalent or octivalent, and the fact that a volatile fluoride of manganese is known which contains at least six

atoms of fluorine to every atom of manganese, indicates that the quantivalence of the element in these compounds cannot be less than six. Indeed, the fluorides illustrate very strikingly the different degrees of quantivalence which manganese may assume, for we have MnF_2, MnF_4, $[Mn_2]F_6$, and MnF_6.

When an intimate mixture of $K\text{-}O\text{-}H$ and MnO_2 is roasted in a current of oxygen gas, the following reaction takes place: —

$$4\,K\text{-}O\text{-}H + 2\,MnO_2 + \text{⓪=⓪} = 2\,K_2{=}O_2{=}MnO_2 + 2\,\boxed{H}_2\text{⓪}. \quad [225]$$

On dissolving the resulting mass in water, and evaporating the *deep green* solution thus obtained (*in vacuo*), crystals are formed isomorphous with $K_2{=}O_2{=}SO_2$, in which the hexad atoms of manganese act as acid radicals, and we call the product potassic manganate. The acid corresponding to this compound has never been isolated, and only a few of its salts are known. They are all, like potassic manganate, exceedingly unstable.

On boiling a solution of potassic manganate, the following remarkable reaction results: —

$$(3\,K_2{=}O_2{=}MnO_2 + 3\,H_2O + Aq) =$$
$$MnO_2\,.\,H_2O + (K_2{=}O_2{=}[Mn_2]O_6 + 4\,K\text{-}O\text{-}H + Aq); \quad [226]$$

and a new compound called potassic permanganate is formed, in which the atoms of manganese appear to have a quantivalence of eight. The reaction takes place more readily if a stream of CO_2 is passed through the boiling solution to neutralize the $K\text{-}O\text{-}H$ as it forms, and when the solution is not too strong the carbonic dioxide of the atmosphere will in time determine the same change, even at the ordinary temperature. The solution of $K_2{=}O_2{=}[Mn_2]O_6$ has a *deep violet* color, and the changing tints, during the reaction just described, present a very striking phenomenon. Hence the crude potassic manganate, obtained by melting together MnO_2 and $K\text{-}O\text{-}NO_2$, is commonly known as chameleon mineral; and the production of the characteristic green color, under similar conditions in a blowpipe bead, is the best evidence of the presence of manganese.

Potassic permanganate, prepared as above, may be readily crystallized, and its crystals are isomorphous with those of potassic perchlorate; that is, $K_2{=}O_2{=}[Mn_2]_{\text{III}}O_6$, or possibly $K\text{-}O\text{-}Mn\equiv O_3$, has the same form as $K\text{-}O\text{-}Cl\equiv O_3$. From potassic permanganate a number of other

permanganates may be prepared, and also permanganic acid, a dark-colored volatile liquid. Permanganic acid is formed when the solution of a manganese salt is boiled with nitric acid and plumbic dioxide, and a violet color developed in the liquid under these conditions is a certain indication of the presence of manganese. The permanganates are more stable than the manganates, but still they readily part with a portion of their oxygen, and act as powerful oxidizing agents. A solution of potassic permanganate is much used for this purpose in the laboratory. For example, it changes ferrous into ferric salts.

$$(10\,Fe''O_2''SO_2 + K_2''O_2''[Mn_2]O_6 + 8\,H_2''O_2''SO_2 + Aq) =$$
$$(5\,[Fe_2]'''O_6'''[SO_2]_3 + K_2''O_2''SO_2 + 2\,Mn''O_2''SO_2 + 8\,H_2O + Aq). \quad [227]$$

The slightest excess of the permanganate is at once indicated by the color it imparts to the liquid, and the reaction is the basis of one of the most valuable methods of volumetric analysis. Both the manganates and the permanganates are at once decomposed by all organic tissues, which they rapidly oxidize, and a crude sodic permanganate is much used as a disinfecting agent. Potassic permanganate in boiling alkaline solution decomposes albumen with evolution of a certain amount of the nitrogen as ammonia, and on this reaction is founded a common method of water analysis.

264. **IRON.** $Fe = 56$. — Usually bivalent or quadrivalent, but rarely sextivalent. A universally diffused element, and the most abundant and important of the useful metals. As an accessory ingredient, it enters into the composition of almost every substance, and it is the chief metallic radical of a very large number of important minerals.

Oxides.

MAGNETITE,	Isometric,	$Fe''[Fe_2]'''O_4$,
Magnesioferrite,	Isometric,	$Mg''[Fe_2]'''O_4$,
FRANKLINITE,	Isometric,	$[Zn'', Mn'']_2[Fe_2]'''O_4$,
HEMATITE,		$[Fe_2]'''O_3$
Specular Iron,	Hexagonal.	
Red Hematite,	Massive.	
Clay Iron-stone,	Massive.	
Red Ochre,	Massive.	
MENACCANITE,		$(Ti''Fe'')O_3$
Titanic Iron,	Hexagonal.	

Hydrates.

Limnite,	Massive,	$[Fe_2]^{\equiv}O_6^{\equiv}H_6$
Xanthosiderite,	Massive,	$O^{=}[Fe_2]^{\equiv}O_4^{\equiv}H_4$
Göthite,	Orthorhombic,	$O_2^{\equiv}[Fe_2]^{=}O_2^{=}H_2$
LIMONITE,		$O_3^{\equiv}[Fe_2]_2^{\equiv}O_6^{\equiv}H_6$
Brown Hematite,	Massive.	
Brown Clay Iron-stone,	Massive.	
Bog Ore,	Massive.	
Yellow Ochre,	Massive.	

Carbonates.

SIDERITE,		$Fe^{=}O_2^{=}CO$
Spathic Iron,	Rhombohedral.	
Clay Iron-stone (of the coal-beds),	Massive.	
Sphærosiderite,	Concretionary.	
Mesitite,	Rhombohedral,	$[Mg,Fe]^{=}O_2^{=}CO$
Ankerite,	Rhombohedral,	$[Mg,Fe],Ca^{=}O_4^{\equiv}(CO)_2$

Sulphides.

Troilite,	Massive,	FeS
Magnetic Pyrites,	Hexagonal,	Fe_7S_8 or Fe_9S_{10}?
Iron Pyrites,	Isometric,	FeS_2
Marcasite,	Orthorhombic,	FeS_2
Mispickel,	Orthorhombic,	$Fe^{=}[S_2,[As_2]]$

Sulphates.

Green Vitriol,	Monoclinic,	$H_2,Fe^{=}O_4^{\equiv}SO.6H_2O$
Pisanite,	Monoclinic,	$H_2,[Fe,Cu]^{\equiv}O_4^{\equiv}SO.6H_2O$
Coquimbite,	Hexagonal,	$[Fe_2]^{\equiv}O_6^{\equiv}[SO_2]_3.9H_2O$
Jarosite,	Rhombohedral,	$4(O_2^{\equiv}[Fe_2]^{=}O_2^{=}SO_2).([K,Na]^{=}O_2^{=}SO_2).9H_2O$
Copiapite,	Hexagonal?	$O^{=}[Fe_2]_2^{\times}O_{10}^{\times}[SO_2]_5.12H_2O$
Raimondite,	Hexagonal,	$O_3^{\equiv}[Fe_2]_2^{\equiv}O_6^{\equiv}[SO_2]_3.7H_2O$
Glockerite,	Massive,	$O_2^{\times}[Fe_2]_2^{=}O_2^{=}SO_2.6H_2O$
Fibroferrite,	Fibrous,	$O_4^{\text{VIII}}[Fe_2]_3^{\times}O_{10}^{\times}[SO_2]_5.27H_2O$
Botryogen,	Monoclinic,	$O_4^{\text{VIII}}[Fe_2]_3^{\times}O_{10}^{\times}[SO_2]_5.3Fe^{=}O_2^{=}SO_2.36H_2O$
Voltaite,	Isometric,	$Fe,[Fe_2]^{\text{VIII}}O_3^{\text{VIII}}[SO_2]_4.24H_2O$

Phosphates and Arseniates.

Triphylite,	Orthorhombic,	$[Fe, Mn, Li_2]^{II}_3 O^{II}_2 (PO_4)_2$
Vivianite,	Monoclinic,	$Fe^{II}_3 O^{II}_2 (PO_4)_2 . 8 H_2O$
Dufrenite,	Orthorhombic,	$O^{III}_3 [Fe_2]^{III}_2 O^{II}_2 (PO_4)_2 . 3 H_2O$
Cacoxenite,	Radiated,	$O^{III}_3 [Fe_2]^{III}_2 O^{III}_3 (PO_4)_2 . 12 H_2O$
Scorodite,	Orthorhombic,	$[Fe_2]^{III} O^{III}_3 (AsO_4)_2 . 4 H_2O$
Pharmacosiderite,	Isometric,	$O^{III}_3 [Fe_2]_4^{XVIII} O_{15}^{XVIII} (AsO_4)_6 . 15 H_2O$

Silicates.

Fayalite (Iron Olivine),	Orthorhombic?	$Fe^{II}_2 O^{II}_2 SiO_4$
Ilvaite (Yenite)	Orthorhombic,	$R^{II}_3, [R_2]^{VIII} O_{12}^{VIII} Si_6 O_{18}$
Schorlomite,	Massive,	$Ca_4, [Fe_2]^{XIV} O_{14}^{XIV} [Ti, Si]^{IV}_3 O_{12}$

Compare also Columbite, Tantalite, and Wolfram (§§ 378 and 187).

265. **Metallurgy of Iron.** — Native iron of meteoric origin is not unfrequently found, but it is doubtful whether native iron of terrestrial origin exists, although instances of its occurrence have been reported. The commercial value of the metal is so small that only those ferriferous minerals which are at the same time rich, abundant, readily accessible, and easily smelted, can be utilized as ores. The useful ores, which are all either oxides, hydrates, or carbonates, are distinguished, in the list of iron minerals given above, by a difference of type; and the names of the most important varieties of the different ores follow the names of the species to which they belong. These ores are found either in veins or in beds, associated with rocks of all ages and of very various characters, and the value of a given deposit frequently depends quite as much on its association with coal and lime, and on its proximity to a commercial centre, as on the richness of the ore. Hence the great wealth which has been drawn from the deposits of clay iron-stone in the coal-beds of England, an ore which, intrinsically, is comparatively poor.

All the useful ores of iron, when not anhydrous oxides, are converted into this condition by roasting, and the oxides are easily reduced to the metallic state by simply heating the roasted ore with coal. The smelting process, however, also involves the fusion of the other mineral matter (gangue), with which the true ore is always mixed. This gangue will seldom fuse by itself, even at the high temperature of a blast furnace, and it is almost always necessary to mix the ore with

some *flux* (usually limestone), which will unite with the gangue and form a fusible *slag*. The same end is sometimes attained, or at least an advantage is gained, by mixing different ores.

If the iron is reduced at a comparatively low temperature, as in a *bloomary forge*, the metal separates from the melted slag as a loosely coherent, spongy solid, the *bloom*, and is subsequently rendered compact by hammering and rolling while still at a welding heat. If the iron is reduced at a high temperature, as in a *blast furnace*, the metal unites with a small proportion of carbon and is thereby rendered fusible. Both the fused metal and the melted slag then drop together into the *crucible* of the furnace, and there the difference of density determines a perfect separation of the two molten liquids. The product of the first process is nearly a pure metal, and is called *wrought-iron*. The product of the second process contains a variable amount of carbon (from 2 to 5 per cent), and is known as *cast-iron*.

With the outward aspects of these two varieties of iron every one is familiar. Wrought-iron is so soft that it can be readily worked with files and other steel tools. It is very tough, and has great tenacity. It is exceedingly ductile and malleable. It readily fuses before a compound blowpipe, and in small quantities may even be melted in a wind-furnace. It however requires, for its perfect fusion, a full white heat. But at a lower temperature it becomes soft and pliable, and in this condition can be *wrought* or welded on an anvil. It has a fibrous structure, but this is in a great measure due to the mechanical treatment it receives.

Cast-iron, on the other hand, has a granular or crystalline structure. It is much harder than wrought-iron, and proportionally more brittle. It is therefore neither malleable nor ductile, and cannot be wrought on the anvil like the former metal; but, as it melts at a much lower temperature, it is suitable for *castings*. Cast-iron differs greatly in quality, and the two extreme conditions are seen in the two commercial varieties known as *white iron* and *gray iron*. White iron has a brilliant white lustre and a lamellar crystalline fracture, is very brittle, and so hard that it cannot be worked with steel tools. It is, therefore, not suitable for casting, but may be used to advantage for making wrought-iron or steel. Gray iron has a darker lustre and a more granular fracture. It is much softer, and may be filed, drilled, or turned in a lathe. Although less fusible than white iron, it flows more freely when melted, and is better adapted for casting. It also contains, as a rule, less car-

bon, but the difference of qualities seems to depend more on the condition of the carbon than on the amount. In white iron *all* the carbon appears to be chemically combined with the metal, while in gray iron *the greater part* is disseminated in an uncombined form through the mass.* A form of white iron, called by the Germans *spiegeleisen* (mirror iron), which crystallizes in flat, brilliant tables, and contains about five per cent of carbon, has approximately the composition CFe_4, and another crystalline variety has been described, which nearly corresponds to CFe_8; but the existence of these compounds cannot be regarded as proved. Spiegeleisen, moreover, is not a pure ferro-carbide, but always contains manganese, the amount varying from four to twelve per cent. Indeed, manganese is a very common ingredient of cast-iron, as might be anticipated, seeing that manganesian minerals are so frequently associated with iron ores. Cast-iron also contains variable quantities of silicon, sulphur, and phosphorus, besides traces of other metals, such as aluminum, calcium, and potassium.

By melting cast-iron on the hearth of a reverberatory furnace, the carbon and the other impurities may be more or less thoroughly burnt out, and the metal converted into wrought-iron. At the same time a portion of the iron is oxidized, and a very fusible slag is formed by the union of the oxide with the silica always present.

The metal thickens as it becomes decarbonized, and the spongy *bloom* thus formed is easily separated from the melted slag, and hammered or rolled into bars, as before described. The greater part of the wrought-iron of commerce is made in this way, and the process is called "puddling," because the melted metal is stirred or puddled on the hearth of the furnace in order to expose the mass more effectually to the action of the air. The purest iron thus prepared still contains a small amount of carbon, which does not, however, impair its useful qualities. The other impurities of cast-iron, when not wholly removed, render the wrought-iron friable or brittle (*short*, in technical language), and are highly prejudicial. Sulphur makes the metal friable while hot (*red short*), while phosphorus and silicon make it brittle when cold (*cold short*).

* When the fracture exhibits large, coarse grains, among which points of graphite are distinctly visible, the metal is said to be *mottled*. Mottled iron is very tough, and is especially valued for casting ordnance. Of all three varieties of cast-iron, — the white, the mottled, and the gray, — the iron-masters distinguish several grades.

That most valuable form of iron called steel holds an intermediate position between wrought- and cast-iron, and partakes, to a great extent, of the valuable qualities of both. At a white heat it may be worked on the anvil, like wrought-iron, and at a higher temperature, but still, within the range of a wind furnace, it may be melted and cast. If suddenly quenched in water, when red-hot, it becomes as hard and brittle as white cast-iron; and when subsequently heated to a regulated temperature, the *temper* may be reduced to any desired extent. It may thus be made soft and tough, or hard and elastic, at will, and on this remarkable quality its numerous and important applications to the useful arts depend. Good steel contains from 0.7 to 1.7 per cent of carbon, and it is made either by carbonizing wrought-iron, as in the ordinary *cementation* method, or, as in the Bessemer process, by decarbonizing cast-iron; but it is probable that the qualities of steel depend fully as much on some unknown causes as on the presence of carbon. It has even been doubted whether the presence of carbon is essential; and, indeed, the whole subject is very obscure.

266. **Metallic Iron.** — The *Sp. Gr.* of the purest iron is 8.14, but cast-iron has sometimes a specific gravity as low as 7, and the density of the different varieties of the metal ranges between these extremes, the average for good bar-iron being 7.7. Iron is distinguished for its great susceptibility to magnetism, and in this respect it far surpasses both nickel and cobalt, the only other metals that exhibit this property in any marked degree. The susceptibility of iron to magnetic induction diminishes as its hardness increases, but at the same time its power of retaining the virtue is enhanced. Thus, iron can only be permanently magnetized when combined with carbon, as in steel, or with oxygen, as in the magnetic oxide or loadstone, Fe_3O_4, or with sulphur, as in magnetic pyrites, Fe_7S_8; but it is a fact worthy of notice, that spiegeleisen, specular iron, Fe_2O_3, and common pyrites, FeS_2, are almost indifferent to the action of a magnet, and the same is true of most other iron compounds.

At a high temperature iron burns readily, and under favorable conditions will sustain its own combustion (§ 68). The product formed is Fe_3O_4. At a red heat it also decomposes water, yielding the same oxide as before, together with hydrogen gas. At the ordinary temperature, however, polished iron retains its lustre unimpaired, both in *dry* air and in *pure* water (free from air); but when exposed to both air and moisture, the surface soon becomes covered with rust. Moreover,

this change is not merely superficial, but under favorable conditions proceeds until the whole mass of the metal is converted into a ferric hydrate, having the composition of Limonite. The change accelerates as it advances, and the rust first formed seems to act as a carrier of oxygen to the rest of the metal. The corrosion of wood and other organic fibre, when in contact with rusty nails, has been explained in a similar way. It is also a favorite theory that a coating of rust forms with the metal a voltaic combination, which actually decomposes the water present, and this is thought to account for the singular fact that iron-rust always contains ammonia.

Iron readily dissolves in dilute mineral acids, yielding a ferrous salt and hydrogen gas. It also dissolves in aqueous solution of carbonic acid if free from air. Concentrated sulphuric acid, even when boiled with iron, has but little action upon it. Nitric acid, on the other hand, rapidly dissolves the metal with evolution of *NO*. It is a singular fact, however, that the most concentrated nitric acid (*Sp. Gr.* 1.45) not only does not attack iron, but so modifies its condition that it may subsequently be kept for weeks in acid of the ordinary strength (*Sp. Gr.* not less than 1.35) without the slightest alteration of the polish on its surface. This same *passive condition* may also be induced in other ways.

Iron enters into chemical combination with almost all the non-metallic elements, and forms alloys with many of the metals. Corresponding to the three degrees of quantivalence are three very distinct classes of compounds: first, the *ferrous* compounds, whose radical is a single bivalent atom of iron; secondly, the *ferric* compounds, having a sextivalent radical consisting of two quadrivalent atoms of iron; and lastly, a few very unstable salts called *ferrates*, analogous to the manganates, in which a sextivalent atom of iron is the acid radical. The last class of compounds, although practically unimportant, are interesting, as they indicate the close relationship between iron and manganese; but iron differs from all the elements with which it is allied in that the two radicals Fe'' and $[Fe_2]^{VI}$ form equally stable compounds, and play an equally important part in the mineral kingdom; and this double aspect of the element is one of its most characteristic and important features.

267. **Ferrous Compounds.** — The crystallized ferrous compounds have, as a rule, a light green color, and ferrous oxide imparts the same color to glass. The soluble ferrous salts have a characteristic styptic

taste. They are isomorphous with the corresponding compounds of magnesium and zinc, and quite as closely allied to them as to those of manganese, cobalt, and nickel, — the elements with which iron is classed in the scheme of this book. Thus, in nature, ferrous carbonate is as intimately associated with the carbonates of magnesium and zinc as with the carbonate of manganese, and the four bivalent radicals replace each other in almost every proportion, not only in the carbonates, but also in the silicates, and in a large number of other minerals. In like manner, ferrous sulphate (green vitriol), like the sulphates of the same metals, and also those of nickel and cobalt, crystallizes with seven molecules of water, and forms double salts with the sulphates of the alkaline metals (§§ 222, 231, 261). The sulphate is the most important of the soluble ferrous salts, but all the following are also well known: —

Ferrous Chloride,	$Fe\,Cl_2 \cdot 4\,H_2O$
Ferrous Nitrate,	$Fe{=}O_2{=}(NO_2)_2 \cdot 6\,H_2O$
Ferrous Sulphate,	$Fe{=}O_2{=}SO_2 \cdot$ (7, 4, 3, or 2 H_2O)
Ferrous Oxalate,	$Fe{=}O_2{=}C_2O_2 \cdot 2\,H_2O$
Ferrous Phosphate,	$H,Fe{=}O_3{=}PO$

In solutions of the ferrous salts, when protected from the air, the alkaline hydrates give a white precipitate of ferrous hydrate, $Fe{=}O_2{=}H_2$, and the alkaline carbonates a similar white precipitate, which is a hydrocarbonate of variable composition. In the presence, however, of a large amount of NH_4Cl, neither ammonia nor ammonic carbonate gives any precipitate, and the precipitation by the other alkaline reagents is in great measure prevented. The alkaline sulphides, nevertheless, precipitate the iron wholly as a hydrated ferrous sulphide, and so does also H_2S when the solution is alkaline, but not when the slightest excess of any mineral acid is present. Solutions of the ferrous salts, when exposed to the air, absorb oxygen, and the ferrous changes into a ferric compound. The same is true of the ferrous precipitates formed as just described, all of which are very rapidly oxidized as soon as they are exposed to the atmosphere. The products in any case are determined by various conditions, but the following are some of the most characteristic of the reactions: —

$$(4\,Fe{=}O_2{=}SO_2 + 2\,H_2{=}O_2{=}SO_2 + Aq) + \text{O}{=}\text{O} = (2[Fe_2]{\equiv}O_6{\equiv}(SO_2)_3 + 2\,H_2O + Aq). \quad [228]$$

$$(20\,Fe{=}O_2{=}SO_2 + 6\,H_2O + Aq) + 5\,\textcircled{O}{=}\textcircled{O} =$$
$$2\,(O_5{}^{x}[Fe_2]_2{=}O_2{=}SO_2\,.\,3\,H_2O) + (6[Fe_2]^{\equiv}O_6^{\equiv}(SO_2)_3 + Aq). \quad [229]$$

$$4\,Fe{=}O_2{=}H_2 + \textcircled{O}{=}\textcircled{O} = 2\,O{=}[Fe_2]^{\equiv}O_4{=}H_4\,. \quad [230]$$

268. **Ferric Compounds.** — Ferric oxide, when dissolved in melted borax, imparts to the glass a yellow or yellowish-red color, and most of the ferric compounds affect the same tints. They are isomorphous with the corresponding compounds of aluminum, and closely allied to them in their chemical relations. The following are the most important of the soluble normal salts: —

Ferric Chloride, $[Fe_2]^{\equiv}Cl_6\,.\,6\,H_2O$, also with 5 or 12 H_2O
Ferric Nitrate, $[Fe_2]^{\equiv}O_6^{\equiv}(NO_2)_6\,.\,18\,H_2O$, also with 12 H_2O
Ferric Acetate, $[Fe_2]^{\equiv}O_6^{\equiv}(C_2H_3O)_6 + Aq$
Ferric Sulphate, $[Fe_2]^{\equiv}O_6^{\equiv}(SO_2)_3\,.\,9\,H_2O$
Diammonio-ferric Sulphate, $(NH_4)_2,[Fe_2]^{\text{VIII}}O_8{}^{\text{VIII}}(SO_2)_4\,.\,24\,H_2O$
Ferric Oxalate, $[Fe_2]^{\equiv}O_6^{\equiv}(C_2O_2)_3$
Sodio-ferric Oxalate, $Na_6,[Fe_2]^{\text{XII}}O_{12}{}^{\text{XII}}(C_2O_2)_6\,.\,6\,H_2O$

Ferric acetate cannot be crystallized, and the ferric salts, as a rule, crystallize with difficulty. All the well-marked radicals of the type $[R_2]^{\equiv}$ manifest a very strong tendency to form basic compounds (§ 39 and [47]), and the ferric salts furnish a striking illustration of the general principle. Most of the native ferric salts are basic, and the symbols of a number of such compounds have already been given. Their mutual relations will be best understood if they are studied in connection with the various hydrates, from which they may be regarded as derived, and a table of the possible ferric hydrates is easily made after the principle of § 131. Of the compounds which are thus theoretically possible, a large number are easily prepared, and a still larger number are at times formed when the conditions happen to be favorable; but as the compounds become more basic, they soon lose every trace of crystalline structure, and with this all evidence of definite chemical constitution disappears. The products are then amorphous or colloidal solids, which present in their composition every possible gradation between certain limits.*

* Solutions of various basic compounds are readily obtained, either by dissolving freshly precipitated ferric hydrate in a solution of almost any ferric salt, or by partially abstracting the acid of the salt by the cautious addition of an alkali. A solution of ferric nitrate, for example, may thus be made to take up seven additional atoms of $[Fe_2]$. On allowing such solutions to evaporate spontaneously, the basic compounds may frequently be obtained in the solid state.

All the more basic salts are, as a rule, insoluble in water, but in several cases they affect both a soluble and an insoluble modification, and under certain conditions the first changes into the last on simply boiling the solution. The soluble condition appears in all cases to be a colloidal modification, and by dialyzing (§ 61) a solution of basic ferric chloride it is possible to remove almost all the acid radical, and obtain nearly a pure solution of ferric hydrate. This solution coagulates on standing, and the ferric hydrate thus passes through successive stages of dehydration. On boiling the water, the dehydration proceeds still further, until at last a hydrate corresponding to Göthite is formed. So also the voluminous hydrate, first precipitated by alkaline reagents from cold solutions of ferric salts, undergoes a similar change under the same conditions. These facts would lead us to infer that the "coagulation" of the solutions of the basic ferric salts is caused by the elimination of a certain quantity of water from the molecules of the compounds.

The ferric compounds, although permanent in the air, are easily reduced to the ferrous condition by the feeblest reducing agents.

$$([Fe_2]Cl_6 + Aq) + Zn = (2\,FeCl_2 + ZnCl_2 + Aq). \quad [231]$$

$$([Fe_2]Cl_6 + H_2S + Aq) = S + (2\,FeCl_2 + 2HCl + Aq). \quad [232]$$

In solutions of ferric salts, the alkaline hydrates and carbonates all give a red precipitate of ferric hydrate, whose constitution varies with the conditions of the experiment, as indicated above. *This precipitate is insoluble in an excess of sodic or potassic hydrate.* In the same solutions potassic sulphocyanate strikes a deep red color, and potassic ferrocyanide gives a deep blue precipitate. These reactions are very delicate, and enable us to detect the smallest amount of a ferric compound, even in the solution of a ferrous salt. The ferrous compound, under the same conditions, gives in one case no color, and in the other a white precipitate.

269. **Chlorides.** $FeCl_2$ and $[Fe_2]Cl_6$. — By carefully heating crystallized ferrous chloride (§ 267) out of contact with the air, the anhydrous compound can be obtained; but a solution of ferric chloride cannot be rendered anhydrous by evaporation, since the hydrous compound is decomposed by heat into hydrochloric acid and ferric oxide. Anhydrous ferrous chloride can also be obtained by passing HCl over ignited metallic iron. Anhydrous ferric chloride can be prepared in a similar way, using Cl-Cl instead of HCl. The first

yields a white sublimate; the second, which is the more volatile, is deposited in brownish crystalline scales, and the Sp. Gr. of its vapor has been determined. (Table III.) From this vapor density and the principles of § 35 and § 53, we infer that the molecular structure of this compound is correctly represented by the symbol $Cl_2{=}FeFeCl_2$, and the student should notice that an artiad atom may thus acquire the semblance of a perissad. There are fluorides, bromides, and iodides corresponding to the chlorides, but they have no special interest.

270. **Oxides.** — FeO, $[Fe_2]O_3$, $Fe,[Fe_2]^{VIII}O_4$. — Ferrous oxide may be prepared by boiling in the surrounding water the voluminous white hydrate obtained when an alkali is added to the solution of a pure ferrous salt, every trace of air being carefully excluded. If exposed to the air, it rapidly absorbs oxygen, and $[Fe_2]O_3$ is the final result. A black pyrophoric powder, obtained by igniting ferrous oxalate in a close vessel, is a mixture of the same oxide with metallic iron. Ferric oxide is prepared for the arts by igniting green vitriol, or, still better, ferric sulphate. It forms, even when most highly levigated, a very hard powder, much used for polishing glass and metallic surfaces (Colcothar, Crocus Martis, Rouge). It is also used as a red paint. Ferrous-ferric oxide is formed when either of the other oxides is intensely heated in the air, and must, therefore, be regarded as the most stable of this class of compounds. It is distinguished by its susceptibility to magnetism, and its crystalline form (§ 105), which connects it with Spinel (§ 283) and other allied isomorphous compounds. Besides the above, one or more intermediate oxides have been distinguished, but they are probably mixtures of the oxides already named. As has been already stated, both the oxides and the hydrates are abundant native minerals and important ores.

271. **Sulphides.** — The fusible product obtained by melting together iron and sulphur, and so much used in the laboratory for making H_2S, is essentially ferrous sulphide, FeS, although its composition is not absolutely constant. The same compound may be formed by mixing flowers of sulpnur and iron filings with water, and, since the resulting compound forms a coherent mass, this mixture is useful under certain conditions as a cement. Ferric disulphide, FeS_2 (Iron Pyrites), is by far the most abundant of the native metallic sulphides. It occurs in almost all mineral veins, and is known to the miners as *Mundic*. It is readily distinguished by its yellow color and great hardness. The more compact varieties are very resisting minerals, but those

of a looser texture rapidly crumble when exposed to the atmosphere, and this is especially true of the orthorhombic variety called *Marcasite*. The crumbling of many rocks is also caused by the oxidation of the pyrites which they contain. Although useless as an ore of iron, common pyrites is exceedingly valuable as a source of sulphur, and for the manufacture of sulphuric acid. The magnetic sulphide, Fe_7S_8, has already been mentioned, and there is also a sulphide, Fe_3S_4, corresponding to the magnetic oxide, and another, Fe_2S_3, corresponding to ferric oxide. Moreover, sulphides of the composition Fe_8S and Fe_2S have been formed, but it is doubtful whether they are definite compounds. The black precipitates, obtained when an alkaline sulphide is added to the solutions of ferrous and ferric salts, are either sulphohydrates (§ 175) or molecular compounds of the sulphide and water. They are both very unstable products, and rapidly oxidize when exposed to the air.

272. **Ferrates.** — Potassic ferrate, $K_2{=}O_2{=}FeO_2$, may be prepared either by fusing ferric oxide with nitre, or by passing chlorine gas through a very strong solution of potassic hydrate, in which ferric oxide is suspended. Both the fused mass of the first reaction, and the black powder deposited from the alkaline solution in the second, yield with water a beautiful violet-colored solution of potassic ferrate. This compound is very unstable, and has merely a theoretical interest. Ferrates of the alkaline earths are also known; but neither ferric acid nor any compounds corresponding to the permanganates have as yet been discovered.

QUESTIONS AND PROBLEMS.

Manganese.

1. By what simple blowpipe test may the presence of manganese in a mineral be recognized? How far is the color of the manganese minerals characteristic?

2. Compare the manganous with the nickelous and cobaltous salts, and show to what extent they resemble each other, as well as indicate the points of difference.

3. Compare the ammonio-salts of the same three elements, and seek the cause of the difference of the effects which the atmospheric air produces when solutions of these salts are exposed to its influence.

4. Represent by graphic symbols the constitution both of manganous and manganic alum.

5. Write the reaction of potassic hydrate on a solution of manganous chloride, and the further reaction when the resulting precipitate is exposed to the atmospheric air. Assume that the final product is manganic hydrate.

6. Write the reaction of hydro-disodic phosphate and ammonic hydrate on a solution of manganous chloride, and also indicate the further change which takes place on igniting the resulting precipitate.

7. Make a list of the oxides of manganese, and show how far they correspond to the oxides of nickel and cobalt on the one side, and to those of iron on the other. Make also a similar comparison of the different hydrates. Compare also the different oxides and hydrates as regards their relative stability.

8. Of the metals thus far studied, which are precipitated from acid solutions, and which only from alkaline solutions, by H_2S?

9. By what solvents may the sulphides of manganese, zinc, and cobalt, when precipitated together, be separated?

10. In what other way may manganese, when in solution, be separated from nickel and cobalt?

11. To what relationship does the crystalline form of the native carbonates of manganese point?

12. By what means may manganese be separated from zinc when both are present in the same solution as acetates? If they are in the condition of chlorides, how may they be readily converted into acetates? How far may the same methods be used to separate manganese from the metallic radicals previously studied?

13. Write the reaction of the atmospheric oxygen on a solution of ammonio-manganous chloride.

14. Write the reaction of chlorine gas on manganous carbonate suspended in water.

15. Represent by graphic symbols the constitution of Pyrolusite, Braunite, and Hausmannite, and endeavor to harmonize the crystallographic relations stated above.

16. Represent by graphic symbols the constitution of Manganite and Göthite.

17. Write the reaction of sulphuric and also of hydrochloric acid on each of the three oxides MnO_2, Mn_2O_3, Mn_3O_4.

18. When a mixture of MnO_2 and oxalic acid is heated with dilute sulphuric acid, the products are manganous sulphate, water, and carbonic dioxide gas. Write the reaction, and calculate how much CO_2 would be formed for every gramme of MnO_2 taken.

19. Can you base on the reaction just written a method of determining the purity of the commercial "black oxide of manganese," which is frequently a mixture of the different native oxides, and is sometimes adulterated with sand?

20. Assuming that one gramme of a sample of the commercial oxide sets free, as above, 0.654 gramme of CO_2, how much bleaching salts could be manufactured with 1,000 kilo. of the oxide, assuming that the symbol of the bleaching salts is $(Ca\text{-}O)=Cl_2$?

21. Write the reaction of MnO_2 on $HCl + Aq$, assuming that $MnCl_4$ is first formed and subsequently decomposed by the heat employed.

22. Represent by graphic symbols the constitution of manganic and manganous alum. (§ 263.)

23. State the distinction between the two classes of manganic compounds, and illustrate by representing the constitution of Mn_2O_3, first as a normal sesquioxide, and secondly as a molecular compound of manganous oxide and manganic dioxide.

24. Compare the manganic compounds with the corresponding compounds of nickel and cobalt. Consider in this connection the relative stability of the substances compared.

25. Represent the constitution of potassic manganate by a graphic symbol, and compare this with the graphic symbol of potassic sulphate.

26. How far does the isomorphism of the sulphates with the manganates indicate the quantivalence of the metallic radical in these compounds? What should you infer from the great difference in the stability of the two classes of salts in regard to the sextivalent condition of manganese?

27. Analyze reaction [225], and show that it turns on a change of quantivalence in the manganese atoms.

28. Is it necessary to assume a similar change of quantivalence in reaction [226]?

29. Represent the constitution of potassic permanganate by a graphic symbol, both on the assumption that the atoms are octivalent and also assuming that they are still sextivalent. Can you give any reasons why one symbol should be more probable than the other? Does not the fact that the per-

manganates are more stable than the manganates have a bearing on the question? How can you reconcile the isomorphism of the permanganates and the perchlorates, manganese being an artiad and chlorine a periad element?

30. Write the reaction when a solution of manganous chloride is boiled with free nitric acid and plumbic dioxide.

31. How could reaction [227] be used to determine the amount of iron in a given solution?

32. What do you regard as the chief characteristic of manganese as compared with the allied metallic radicals? And why does the study of its compounds have a peculiarly important bearing on chemical theories?

33. Does not the study of the manganese compounds indicate a more rational use of the terminations *ous*, *ic*, *ite*, and *ate* in the nomenclature of chemistry?

34. How may the principles of the nomenclature stated in Chapter X. be extended so as to express accurately the constitution of the more complex chemical compounds? Give rules based on your own experience, and illustrate them by examples. Bear in mind, however, that, according to the best usage, the Greek numerals are employed, rather than the Latin, as prefixes.

Iron.

35. Compare the native compounds of manganese and iron, and point out the analogies, as well as the differences, which you observe.

36. Compare in the same way the native compounds of nickel and cobalt with those of iron, paying special attention to the sulphides and arsenides.

37. Compare the native compounds of magnesium and zinc with those of iron.

38. The mineral Pisanite indicates what relation between iron and copper?

39. Why is not Pyrites indicated among the ores of iron? State some of the circumstances on which the value of a bed of iron ore depends.

40. The *Sp. Gr.* of Pyrites is 5.2; that of Marcasite, 4.7; and that of Mispickel, 6.2. Compare the molecular volumes of these minerals.

41. Make a table giving the symbols of the minerals isormorphous with Iron Pyrites and Marcasite respectively.

42. Explain the theory of the "Blast Furnace,"* and show that the formation of slags of the right fusibility is essential to the success of the process, and that the proportion of flux must be differently adjusted according as cold or hot blast is used.

43. The slag formed both in the bloomary forge * and in the puddling process * is a *very* fusible *ferrous* silicate, having approximately the composition $Fe_2^{\equiv}O_4^{\equiv}Si$. Explain the theory of these processes, and show that the great fusibility of the slag is an essential condition of the production of wrought-iron. Could the loss of iron in the slag be avoided? How do you account for the low quantivalence of iron in this product? To what mineral does it correspond in composition?

44. Explain the theory of the Bessemer process * for refining cast-iron or making steel, and compare it with the puddling process. Consider especially the effects of the very high temperature attained in Bessemer's converter.

45. Compare the qualities of iron in its three conditions of cast-iron, wrought-iron, and steel.

46. State the differences between the several varieties of cast-iron, — gray, mottled, white, and spiegeleisen.

47. When white iron is dissolved in acid, all the carbon is converted into a volatile hydrocarbon oil, while under similar circumstances gray iron leaves a large residue of graphite. What conclusion do you draw from these facts?

48. Write the reaction when iron burns.

49. Write the reaction when steam is passed over red-hot iron.

50. Write the reaction when iron rusts, assuming, 1st. That the metal draws the oxygen wholly from the air; 2d. That water is decomposed and ammonia formed.

51. Write the reaction of an aqueous solution of carbonic acid on iron, assuming that no air is present. What is the nature of the solution thus obtained (§ 189)?

52. Write the reaction of dilute sulphuric acid on iron, and inquire how much the acid should be diluted in order to obtain the best effect. In preparing ferrous sulphate, why is it best to use ferrous sulphide instead of metallic iron?

53. Write the rational symbol of dipotassio-ferrous sulphate, and compare its constitution with that of the isomorphous ferrous sulphate (§ 267).

* See Roscoe's Chemistry or Percy's Metallurgy.

54. Compare the sulphates of magnesium, zinc, manganese, and iron, as regards the varying quantities of water of crystallization with which the several salts may combine.

55. Pure ferrous nitrate may be obtained by dissolving ferrous sulphide in dilute nitric acid. Write the reaction.

56. When metallic iron is dissolved in dilute nitric acid, the products are ferrous nitrate, ammonic nitrate, and water. Write the reaction, and compare it with the last.

57. Write the reaction of nitric acid (common strength) on iron, assuming that the products are ferric nitrate and nitric oxide.

58. Ferrous phosphate is formed by precipitation on adding common sodic phosphate to the solution of a ferrous salt. Write the reaction.

59. Ferrous oxalate is obtained on adding ammonic oxalate to a solution of ferrous sulphate. Write the reaction.

60. Write the reaction which takes place when sodic hydrate is added to a cold solution of ferrous sulphate, the air being wholly excluded. What further change takes place if the liquid is boiled in which the precipitate is suspended?

61. Write the reaction of ammonic sulphide on a solution of ferrous sulphate, assuming that the precipitate fixes two molecules of water.

62. Write the reaction of sodic carbonate on a solution of ferric sulphate, assuming that the constitution of the product is analogous to that formed when the same reagent is added to a solution of magnesic sulphate.

63. Write the reaction of sodic carbonate on a solution of ferrous chloride first, when the solution is cold ; secondly, when it is boiling.

64. Ferric hydrate dissolves in a solution of acid potassic oxalate, forming potassio-ferric oxalate. Write the reaction. What practical application may be made of it?

65. Normal ferric oxalate is precipitated when a slight excess of any ferric salt is mixed with a solution of ammonic oxalate. Write the reaction. The precipitated ferric oxalate readily dissolves in a solution of oxalic acid. What compound is probably formed? When this solution is exposed to the sun, *ferrous* oxalate is precipitated, and CO_2 is evolved. Write the reaction.

66. A solution of ferrous carbonate in ($CO_2 + Aq$) deposits, when exposed to the air, a hydrate having the composition of Limonite. Write the reaction. Under what circumstances might you expect that a solution of ferrous

carbonate would be formed in nature, remembering that the soil contains more or less ferric hydrate? Under what circumstances would Siderite be deposited from such chalybeate waters (§ 189)? Can you form any theory which accounts for the formation of beds of Siderite (clay iron-stone) in connection with the coal measures?

67. Make a table of the possible ferric hydrates, and point out the relations of the native hydrates in your scheme.

68. By means of the table made as just directed, show in what relation the different native sulphates, phosphates, and arseniates stand to the hydrates.

69. Make a table illustrating how many nitrates, sulphates, or phosphates may be formed corresponding to any one of the possible hydrates.

70. Represent by graphic symbols the constitution of the basic sulphate $O_6[Fe_2]_2{=}O_2{=}SO_2$.

71. When to the solution of a ferric salt an alkali is added until it begins to occasion a permanent precipitate, and the solution is then raised to the boiling point, the whole or the greater part of the iron is precipitated as an insoluble basic salt. How do you explain the reaction?

72. Starting with a molecule of a ferric salt, show what products would result by the assimilation of successive molecules of ferric hydrate. Again, starting with one or more of the complex molecules thus obtained, and eliminating all the possible molecules of water, show what must be the constitution of the basic salts which would then be formed.

73. Have you observed that the solubility of salts in water has any connection with the number of atoms of typical hydrogen they contain? Cite examples in favor of this theory.

74. Cite different cases in which water is eliminated from a molecule on boiling the liquid in which the compound is dissolved or suspended.

75. When anhydrous ferrous sulphate is heated to redness, as in the process of making Nordhausen sulphuric acid (§ 183), it is resolved into ferric oxide and into sulphurous and sulphuric anhydrides. Write the reaction.

76. The Nordhausen acid is now more frequently made by distilling anhydrous *ferric sulphate*. Write the reaction, and show how the sulphate may be regenerated, and the same oxide used over and over again.

77. How could the reactions [231] and [227] be used to determine the relative amounts of the two iron radicals in a given mineral, assuming that it could be brought into solution without changing the atomic condition of the metal?

78. Baric carbonate precipitates all the iron from ferric, but not any of the metal from ferrous solutions. Moreover, ferrous hydrate precipitates ferric hydrate from the solutions of ferric salts. Write these reactions, and discuss the different relations of the two iron radicals to which they point.

79. By what characteristic reactions may the atomic condition of iron, when in solution, be easily determined?

80. Can one condition of iron be said to be more stable *absolutely* than the other?

81. What two wholly distinct relationships does iron manifest? Trace the lines of connection in each case. Point out also the specific character by which iron is related to each member of the two groups of allied elements.

82. By what character is iron chiefly marked?

83. Compare the reaction of $(HCl + Aq)$ on Ni_2O_3, Co_2O_3, Mn_2O_3, Fe_2O_3, and show that the differences depend on the relative stability of the sesquivalent radicals.

84. In what way may magnesium, zinc, nickel, cobalt, and manganese be separated from aluminum, chromium, and iron?

85. Is there any reason for believing that in crystallized ferric chloride the water forms a part of the salt molecule? Write the reaction which takes place when the salt is heated.

86. Does the Sp. Gr. of anhydrous ferric chloride throw any light on the constitution of the ferric salts?

87. Write the reactions of H-Cl and of Cl-Cl on ignited metallic iron. Why should a ferrous compound be formed in the first case, when a ferric compound is formed in the second?

88. When MnO_2 is melted into glass colored green by ferrous oxide, the color is either wholly removed, or, when originally very deep, is changed to yellow. How do you explain this reaction, and also the other familiar blowpipe reactions of ferric oxide with a borax bead.

89. Ferric oxide, obtained by drying the hydrate at a temperature not exceeding 320°, dissolves easily in acids; but if heated to a low red heat, it suddenly glows, becomes denser, and, after this, dissolves in acids with difficulty. Are you acquainted with similar facts in regard to any other metallic oxides? It is observed that the ignited oxide dissolves without difficulty in $(HCl + Aq)$ when the action is aided by ferrous chloride, zinc, stannous chloride, or some other reducing agent. How do you explain the reaction?

90. Write the reaction when FeS_2 is burnt in a current of air, assuming that the products are Fe_2O_3 and SO_2, and calculate how much sulphuric acid, *Sp. Gr.* 1.501, can be made from 1,000 kilo. of Pyrites.

91. In one process of purifying coal gas, the H_2S is absorbed by moist ferric oxide, and the sulphide thus formed is subsequently exposed to the air, when the oxide is "regenerated." Explain the reaction.

92. Pyrites appears to be formed in nature by the deoxidation of calcic sulphate by means of organic matter in presence of chalybeate waters, and crystals have been formed artificially on twigs in solutions of ferrous sulphate. Explain the reaction.

93. When SO_2 is passed through an alkaline solution of potassic ferrate, ferric oxide is precipitated, while potassic sulphate is formed in the solution. Write the reaction, and show that it may be used to determine the constitution of the ferrates.

94. Point out the ferrous and ferric compounds among the symbols in § 264, and determine in each case the ratio which the quantivalence of the acid radical bears to that of the basic radicals, both $R^{=}$ and $[R_2]^{\equiv}$.*

95. The slag of a blast-furnace is essentially a double silicate of aluminum and calcium, in which the total quantivalence of the two basic radicals, $Ca^{=}$ and $[Al_2]^{\equiv}$, is in the ratio of one to two. In the less fusible slags the total quantivalence of all the basic radicals is equal to that of the silicon, while in the most fusible slags it is only one half of that amount. Write the symbols of these silicates, assuming (as is usually the case) that the calcium is partially replaced by magnesium and iron.*

* If found too difficult, these questions may be reserved until Division XXIX., on Silicon, has been studied.

DIVISION XV.

273. **CHROMIUM.** $Cr = 52.2$. — Sometimes, although rarely, bivalent. Usually either quadrivalent or sextivalent. Many of the compounds of this element have a brilliant color, and are used as paints, and the name is derived from χρῶμα (color). The only important native compounds are

Chromite (Chrome Iron),	Isometric,	$Fe,[Cr_2]''O_4$
Crocoite,	Monoclinic,	$Pb''O_2{}^{\cdot}CrO_2$

The first is the ore from which all the chrome pigments used in the arts are indirectly prepared. It has an iron-black color, and has been found in abundance at a few localities, associated with serpentine. The second, although a very rare mineral, is well known on account of its brilliant red color, and in it the element chromium was first discovered (by Vauquelin in 1797).

274. **Metallic Chromium** may be prepared by reducing Cr_2O_3 with carbon at a very high temperature, and still more readily by reducing Cr_2Cl_6 with zinc, magnesium, or the alkaline metals. On account of its very great infusibility, it has never been obtained in compact masses, and its qualities are therefore imperfectly known. The whitish-gray porous mass, formed when the oxide is reduced by carbon, has a *Sp. Gr.* of 5.9. It is, like cast-iron, a combination of the metal with carbon, and consists of grains, which are as hard as Corundum. The crystalline powder, obtained by reducing the chloride with zinc, has a *Sp. Gr.* of 6.81, and is undoubtedly a purer condition of the metal. When in fine powder, chromium takes fire below redness; but in its more compact forms it resists oxidizing agents as well as aluminum, and acts towards the different mineral acids in a similar way.

275. **Chromous Compounds.** — This class includes all those compounds of chromium in which the element is bivalent; but, since its atoms in this condition have still four strong affinities unsatisfied, the compounds of this order are all very unstable. The most important is $CrCl_2$, which is obtained by heating Cr_2Cl_6 to redness in a current of dry hydrogen. The white powder thus formed gives a blue solution with water, which, however, rapidly absorbs oxygen, and becomes green when exposed to the air. Chromous hydrate, which falls as a dark

brown precipitate on adding caustic potash to the blue solution, even decomposes water with evolution of hydrogen. The most stable of the chromous salts is $K_2, Cr{=}O_4{=}[SO_2]_2 \,.\, 6\,H_2O$, which forms beautiful blue crystals isomorphous with the corresponding ferrous salt.

276. **Chromic Compounds.** — In these compounds the element is quadrivalent, but they all contain the sextivalent radical $[Cr_2]$. The commercial chromic oxide is a brilliant green powder, which is very much used in the arts, not only as a common paint (chrome green), but also as a vitrifiable pigment, since it imparts a beautiful green color to glass and to the glazing of porcelain ware. It may be prepared from the chromates in a great variety of ways, as is illustrated by the following reactions: —

$$4\,[Hg_2]{=}O_2{=}CrO_2 = 2\,[Cr_2]O_3 + 8\,Hg + 5\,O{=}O. \qquad [233]$$

$$(NH_4)_2{=}O_2{=}Cr_2O_5 = [Cr_2]O_3 + 4\,H_2O + N{\equiv}N. \qquad [234]$$

$$4\,Cl{=}O_2, Cl_2 = 2\,[Cr_2]O_3 + 4\,Cl{-}Cl + O{=}O. \qquad [235]$$

$$K_2{=}O_2{=}Cr_2O_5 + Cl{-}Cl = [Cr_2]O_3 + 2\,KCl + 2\,O{=}O. \qquad [236]$$

The first two reactions are obtained by simply igniting the solid chromates; the third, by passing the vapor of chloro-chromic oxide through a red-hot porcelain tube; and the last, by passing chlorine gas over ignited potassic dichromate. By the third reaction the oxide may be obtained in definite rhombohedral crystals (*Sp. Gr.* 5.21), which have the form and hardness of specular iron, and even the amorphous commercial oxide is so hard that, when finely levigated, it may be used like rouge for polishing glass. In this hard condition the oxide is almost insoluble in acids. There is, however, a less dense condition of the oxide (obtained by cautiously heating the hydrate), which dissolves freely in all the mineral acids. It has a darker color, and, like ferric oxide, changes suddenly with incandescence into the insoluble modification, if heated above a definite point. At the highest temperatures chromic oxide does not lose oxygen, and cannot be reduced by hydrogen. It may be melted by the heat of a forge fire, and the molten oxide forms, on cooling, a very hard dark green crystalline solid.

There are a number of *chromic hydrates* corresponding to the ferric hydrates; but the different compounds cannot be isolated as readily, and their symbols have not been as accurately determined. When sodic or potassic hydrate is added to the solution of a chromic salt, the chromic hydrate first precipitated is dissolved by an excess of the reagent, but the precipitate reappears on boiling the liquid. These pre-

cipitates retain a portion of the alkali, which modifies the qualities of the hydrate, and this circumstance renders the investigation of these compounds very difficult. The only way to procure a pure hydrate is to precipitate with ammonia from boiling solutions. The light blue precipitate thus obtained retains from one to seven molecules of water, according to the conditions under which it is dried.

The soluble chromic salts affect, as a rule at least, two modifications. In one state they have a violet color, and crystallize more or less readily, while in the other they have a green color, and are uncrystallizable. Thus we have, besides an anhydrous chromic sulphate, which is red and insoluble, the two following hydrous salts: —

Violate Sulphate (soluble and cryst.), $[Cr_2]^{VI}O_6^{II}(SO_2)_3 \cdot 15\,H_2O$
Green " (soluble but uncryst.), $[Cr_2]^{VI}O_6^{II}(SO_2)_3 \cdot 5\,H_2O$

The second is obtained by heating the crystals of the first to 100°. But the water thus driven off cannot be wholly water of crystallization; for on simply boiling a solution of the violet compound, the same change of color and crystalline character takes place. There is evidently an essential alteration in the molecular structure of the compound, but further than this we have as yet no knowledge.

The best known of the chromic salts is *chrome alum*, which is easily prepared from commercial potassic bichromate by the reaction,

$$(K_2{}^{I}O_2{}^{I}Cr_2O_3 + H_2{}^{I}O_2{}^{I}SO_2 + 3\,SO_2 + Aq) = (K_2[Cr_2]^{VIII}O_5{}^{VIII}(SO_2)_4 + H_2O + Aq). \quad [237]$$

This salt, like the other alums, crystallizes with 24 H_2O in octahedrons having a dark purple (nearly black) color, but which, when sufficiently thin, transmit a beautiful ruby-red tint. Care must be taken in reducing the chromate that the temperature of the solution does not rise too high, for above 70° or 80° the change above described takes place, and the salt loses its power of crystallizing. By keeping, however, the green solution thus formed for several weeks, it gradually recovers its violet color, and then will yield the normal crystals.

277. **The Chromic Oxalates** form two interesting series of double salts. Those of the first class have a dark blue, and those of the second class a ruby-red color. Thus we have

Blue Salt, $K_6[Cr_2]^{VI}O_{12}{}^{VII}(C_2O_2)_6 \cdot 6\,H_2O$
Red Salt, $K_3[Cr_2]^{VIII}O_5{}^{VIII}(C_2O_2)_4 \cdot 8\,H_2O$ or $12\,H_2O$

Ammonia gives no precipitate in solutions of these salts, neither does potassic hydrate, until they are boiled. Corresponding compounds are known containing $(NH_4)_2$, Na_2, Ba, Sr, Ca, or Mg, in place of K_2, but with varying quantities of water of crystallization.

278. **Chromic Nitrate** may be obtained in dark purple crystals having the composition $[Cr_2]\dddot{O}_6(NO_2)_6 \cdot 18\ H_2O$, by dissolving chromic hydrate in nitric acid; but the solution becomes green and uncrystallizable if heated beyond a limited degree.

279. **Chromic Chloride**, $[Cr_2]\dddot{Cl}_6$, is prepared by passing chlorine gas through an intimate mixture of chromic oxide with carbon, heated to intense redness in a crucible, when the chloride sublimes and may be condensed in a second crucible covering the mouth of the first. It forms nacreous scales which have a beautiful peach-blossom color, and resist the action of the strongest acids. They are insoluble in cold water, and even in boiling water only dissolve, if at all, very slowly; but singularly, on the formation of the smallest quantity of chromous chloride, (as when touched with zinc,) they dissolve immediately, generating much heat, and forming a *green* solution identical with that obtained by dissolving chromic hydrate in hydrochloric acid. A solution of the corresponding *violet* chloride may be formed by adding baric chloride to a solution of the violet sulphate; and it is worthy of notice, that, while from this last solution argentic nitrate precipitates the whole of the chlorine, it precipitates from a solution of the green compound only one third of its chlorine, unless the liquid is boiled. Green crystals having the composition $[Cr_2]\,Cl_6 \cdot 12\ H_2O$ have been described, and compounds of chromic chloride with the alkaline chlorides are also known.

Besides occurring in the remarkable modifications described above, most of the chromic salts manifest a strong tendency to form basic compounds, but the principle which they illustrate has been already sufficiently discussed (§ 268).

280. **Chlorhydrines.** — When hydrated chromic chloride is dried, it gives off, as the temperature increases, both water and hydrochloric acid, and compounds are formed which occupy an intermediate position between chromic chloride and chromic hydrate, and may be regarded as derived from the former by replacing one or more atoms of chlorine with hydroxyl. Thus we have

Chromic Chloride,	$[Cr_2]\dddot{Cl}_6$
Chromic Penta-chlorhydrine,	$[Cr_2]\dddot{Cl}_5, Ho \cdot 4\ H_2O$

Chromic Tetra-chlorhydrine,	$[Cr_2]^{\text{III}}Cl_4, Ho_2$
Chromic Dichlorhydrine,	$[Cr_2]^{\text{III}}Cl_2, Ho_4$
Chromic Hydrate,	$[Cr_2]^{\text{III}}Ho_6$

The name *chlorhydrines* is now generally applied to bodies of this class, and it can easily be seen that they may be formed from water and the anhydrous chlorides by a simple metathesis. The compounds whose symbols are given in § 435 may be regarded as having a similar constitution, and the same is true of many other oxychlorides, oxyfluorides, &c.

281. **Chromates or Compounds in which Chromium is Sextivalent.** — These are the most characteristic and important of the compounds of this element, and the best known of all is *potassic dichromate*, which is manufactured on a large scale in the arts, and extensively used both in dyeing and in the preparation of various chrome pigments. It is made from native chrome iron, which is reduced to fine powder and roasted on the hearth of a reverberatory furnace with a mixture of chalk and potassic carbonate. The mixture is constantly stirred to hasten the oxidation, and the chalk facilitates the change by retaining the mass in a porous condition. From the product, water dissolves yellow potassic chromate, which is easily converted into the red dichromate by the addition of nitric acid, and the salt is then separated and purified by repeated crystallizations. There are three potassic chromates, all of which yield anhydrous crystals easily soluble in water.

Potassic Chromate (Yellow),	$K_2{=}O_2{=}CrO_2$
Potassic Dichromate (Orange Red),	$K_2{=}O_2{=}Cr_2O_5$
Potassic Trichromate (Dark Red),	$K_2{=}O_2{=}Cr_3O_8$

The normal salt is isomorphous with potassic sulphate. It melts when heated, and is not decomposed by simple ignition; but when heated with reducing agents it yields chromic oxide mixed with some potassic salt. When in solution it has an alkaline reaction, and is converted into the dichromate by the weakest acids. The dichromate also fuses without decomposition, but when heated to a high temperature it is converted into the normal salt and chromic oxide. In solution it has an acid reaction, and on the addition of potassic hydrate changes to the normal salt. Both salts possess great coloring power. The trichromate has merely a theoretical interest.

In another process of manufacturing the commercial chromates the

chrome ore is simply roasted with lime. There is thus formed the normal *calcic chromate*, which, although itself only slightly soluble in water, is converted by digestion with dilute sulphuric acid into a *dichromate*, which is very soluble, and from this solution the other chromate may be easily obtained by simple metathetical reactions. The chromates both of calcium and strontium dissolve readily in dilute acetic acid, while baric chromate is insoluble in this reagent; and on this fact is based an important method of qualitative analysis.

There are two plumbic chromates, which are not only important pigments and dyes, but are also interesting theoretically. Their symbols are usually written thus:—

Plumbic Chromate (Chrome Yellow), $Pb{=}O_2{=}CrO_2$
Diplumbic " (Chrome Orange), $(Pb{-}O{-}Pb){=}O_2{=}CrO_2$

The first falls as a brilliant yellow precipitate when a soluble chromate is added to a solution of plumbic acetate, and corresponds to the mineral Crocoite. It melts at a moderate heat, forming on cooling a red crystalline solid; but when strongly ignited it is decomposed, and a mixture of the second compound with chromic oxide is the result. The diplumbic chromate has a deep orange or red color, according to the mode of preparation. The finest vermilion-red is made by fusing the yellow chromate with nitre, and washing out the potassium salt with water, while an orange color is obtained in dyeing by passing the cloth through boiling lime-water, after chrome yellow has been fixed in its fibres by steeping it successively in solutions of plumbic acetate and potassic bichromate.

Several other metallic chromates, which are easily prepared by precipitation, are used in painting; but the coloring power of the chrome pigments is so great that they are frequently adulterated with chalk or some similar white material, and the tint is varied by mixing them with other paints. One variety of chrome green is a mixture of chrome yellow with Prussian blue.

The chromates are oxidizing agents, and fused plumbic chromate is sometimes used for this purpose in organic analysis. When heated with strong sulphuric acid they evolve oxygen gas [116]; with hydrochloric acid they evolve chlorine, and in both cases chromic salts are formed.

From the chromates we can easily prepare *chromic anhydride*, CrO_3, and the comparative stability of this compound illustrates most mark-

edly the chief characteristic of the element chromium. The anhydride is most readily obtained by pouring one measure of a saturated solution of potassic dichromate into one and a half measures of concentrated sulphuric acid. As the liquid cools, chromic anhydride crystallizes from it in splendid crimson needles. This beautiful compound is permanent in the air, and melts at 190° without undergoing decomposition; but at a higher temperature it gives off oxygen gas, changing first into an intermediate brown oxide, Cr_3O_8, and afterwards into Cr_2O_3. It deliquesces in moist air, and dissolves in water in all proportions. This solution may be regarded as chromic acid, but the solution on evaporation yields crystals of the anhydride, and we have no evidence that a definite compound is formed. It is a very powerful oxidizing agent, and absolute alcohol inflames when brought in contact with the crystals.

Chlorochromic Oxide, $Cr\overset{\equiv}{O}_2, Cl_2$, a compound of the same type as the last, is distilled when a mixture of potassic dichromate, common salt, and sulphuric acid is heated in a glass retort. It is a blood-red volatile liquid, boiling at 118°, and yielding a vapor whose Sp. Gr. (5.52) can be easily determined. It is at once decomposed by water into hydrochloric acid and chromic anhydride, and, like the last, is a powerful oxidizing agent; but it is chiefly interesting from its theoretical bearings. The existence also of $CrCl_6$ and $CrCl_4$ has been inferred from certain reactions, but they have never been isolated.

When potassic dichromate is dissolved in moderately strong hydrochloric acid at a gentle heat, there separate, on cooling, beautiful orange-colored needles of a salt whose composition may be represented by the symbol $Cr\overset{\equiv}{O}_2, Cl, KO$, or $K\text{-}O\text{-}(Cr\overset{\equiv}{O}_2, Cl)$, and another compound has been obtained whose symbol has been written $Cr\overset{\equiv}{O}_2, Cl, Ho \,.\, 2\,H_2Cl$. Their theoretical relations are obvious.

Another interesting compound belonging to the type of chromic anhydride is the fluoride CrF_6. It distils when a mixture of fluor-spar, plumbic chromate, and sulphuric acid is heated in a leaden retort, and may be condensed (in a perfectly dry leaden receiver kept at a very low temperature) to a blood-red liquid; but the moment it comes in contact with moist air it is decomposed into hydrofluoric acid and chromic anhydride, and this reaction is one means of preparing the anhydride in a state of purity.

Lastly, there appears to be a perchromic acid corresponding to the permanganic acid. The compound in question is formed when to a

solution containing peroxide of hydrogen and free hydrochloric or sulphuric acid is added a small quantity of some chromate. On shaking up the mixture with a few drops of ether, this solvent acquires a deep blue color, which is supposed to be due to perchromic acid, and the reaction serves as a very delicate test for chromium.

282. **Sulphides.** — The sulphides of chromium are unimportant. The black precipitate formed when ammonic sulphide is added to the solution of a chromous salt is probably CrS. A sesquisulphide, Cr_2S_3, may also be obtained as a black powder by passing H_2S over ignited Cr_2Cl_6. Like aluminic sulphide, it is decomposed by water, and cannot, therefore, be formed in an aqueous solution.

QUESTIONS AND PROBLEMS.

1. In what order would you classify the elements allied to chromium, regarding only the stability of the compounds in which they act as bivalent radicals? Make a table illustrating this point.

2. In what order would you classify the same elements, regarding alone the stability of the several radicals [R_2]? Compare the qualities of the several oxides and chlorides of these radicals.

3. What is the chief chemical characteristic of chromium? and how is this illustrated by reactions [233 to 236]?

4. Can you form any theory as to the cause of the difference between the blue and green modifications of the chromic salts? Compare § 268.

5. Blue chromic oxalate is made by boiling a solution of 19 parts of potassic dichromate, 23 of potassic oxalate, and 55 of crystallized oxalic acid. The red salt is made in the same way with 19 parts of the dichromate, and 55 of oxalic acid only. Write the reactions.

6. What inference would you draw from the peculiar reactions of chromic chloride?

7. Explain the two methods of making potassic dichromate, and illustrate the processes by reactions.

8. Represent by graphic symbols the constitution of the three potassic chromates.

9. The plumbic chromates may all be represented as containing the radical ($O{=}Pb_2$), including the very rare mineral Phœnicochroite, which contains

23.1% CrO_3 and 76.9% PbO. Write the symbols of the three chromates on this assumption, and weigh their probability as compared with those given above. Compare the reactions of the plumbic with those of the potassic salts, and consider what bearing the general isomorphism of the chromates with the sulphates has on the question (§ 205).

10. Illustrate by reactions the method of dyeing cloth with chrome orange.

11. Write the reaction of strong hydrochloric acid on potassic dichromate, assuming that the principal products are chromic chloride and chlorine gas.

12. When H_2S is passed through a solution of potassic dichromate supersaturated with sulphuric acid, sulphur is precipitated, and the color changes from red to green. Write the reaction.

13. A solution of potassic dichromate supersaturated with sulphuric acid is much used instead of nitric acid in the porous cup of the Grove or the Bunsen voltaic cell (§ 97). What is the theory of its action?

14. When a solution of potassic dichromate supersaturated with sulphuric acid is boiled with oxalic acid, all the chromic acid is reduced to the condition of a chromic salt, and an equivalent amount of CO_2 is set free. Write the reaction, and show how it may be used to determine the quantity of CrO_3 in the dichromate.

15. The chromium in a soluble chromate may also be estimated as sesquioxide. By what reactions may this oxide be separated in a condition to be accurately weighed?

16. How may potassic chromate be used to separate barium from calcium and strontium?

17. It has been found by careful experiment that 10 grammes of chromic anhydride yield 7.6048 grammes of chromic oxide. We know also the Sp. Gr. of chlorochromic anhydride, and that this compound when brought in contact with water undergoes the change described above. Deduce the atomic weight of chromium, and state the steps in your reasoning.

18. Write the reaction by which chlorochromic oxide is obtained in the reaction described in the text. It may also be made by distilling in a small retort a dry mixture of ferric chloride and chromic oxide. Write the reaction.

19. What is the relation of the compound $KCrO_3Cl$ to potassic chromate on the one side, and chlorochromic oxide on the other?

20. Write the reaction by which CrF_6 is obtained in the reaction described above. It may also be prepared by distilling a mixture of potassic dichromate, ammonic fluoride, and sulphuric acid. Write the reaction.

21. Chromic fluoride is decomposed by glass, and for this reason we have not been able to analyze it, or to determine the density of its vapor satisfactorily. Its constitution is inferred from the products of its reaction with water. Is the conclusion trustworthy?

22. Write the reaction of ammonic sulphide on a solution of chrome alum.

DIVISION XVI.

283. **ALUMINUM.** $Al = 27$. — Quadrivalent, but its compounds all contain the double atom $[Al_2] = 54$, which is a sextivalent radical. A very widely distributed element, and, after oxygen and silicon, the most abundant constituent of the rocky crust of the globe, of which it has been estimated that it forms about one twelfth. It occurs chiefly in combination with oxygen and silicon, and most of the siliceous minerals and rocks, when not pure silica, contain aluminum as an essential ingredient. For a full enumeration of the aluminum minerals, the student must consult works on mineralogy. The following list comprises only such of the more characteristic native compounds as illustrate the chemical relations of the element.

Fluorides.

Cryolite,	Orthorhombic,	$[Al_2]F_6 . 6\,NaF$
Chiolite,	Tetragonal,	$[Al_2]F_6 . 3\,NaF$
Pachnolite,	Monoclinic,	$[Al_2]F_6 . 3\,[Ca,Na_2]F_2 . 2\,H_2O$
Thomsenolite,	Monoclinic,	$[Al_2]F_6 . 2\,[Ca,Na_2]F_2 . 2\,H_2O$

Oxides.

Spinel (Ruby),	Isometric,	$Mg,[Al_2]=O_4$
Gahnite,	Isometric	$Zn,[Al_2]=O_4$
Hercynite,	Isometric,	$Fe,[Al_2]=O_4$
Corundum, *Sapphire*, Oriental Ruby, Oriental Topaz, Oriental Amethyst, &c.,	Hexagonal,	$[Al_2]O_3$
Emery,	Massive,	$[Fe_2,Al_2]O_3$

Hydrates.

Gibbsite,	Hexagonal,	$[Al_2]O_3H_6$
Beauxite,	Massive,	$O=[Fe_2,Al_2]O_3H_6$
Diaspore,	Orthorhombic,	$O_2[Al_2]=O_3H_2$

Sulphates.

Alunogen,	Monoclinic,	$[Al_2]^{vi}O_6^{vi}(SO_3)_3 . 18\,H_2O$
Aluminite,	Massive,	$O_2^{vi}[Al_2]=O_2=(SO_2) . 9\,H_2O$
Paraluminite	Massive,	$O_2^{vi}[Al_2]_2=O_2=(SO_2) . 15\,H_2O$
Alum-stone (Alunite),	Rhombohedral,	$K_2,[Al_2]_3{}^{vi}{}_{xx}O_{2,xx}(SO_2)_3,H_{12},\alpha$ $3\,(O_2^{vi}[Al_2]=O_2=SO_2) . K_2=O_2=SO_2 . 6\,H_2O$

Octahedral Alums.

Potassium Alum,	Isometric,	$K_2,[Al_2]^{VIII}O_8^{VIII}(SO_2)_4 \cdot 24\,H_2O$
Ammonium Alum,	Isometric,	$(NH_4)_2,[Al_2]^{VIII}O_8^{VIII}(SO_2)_4 \cdot 24\,H_2O$

Fibrous Alums.

Pickeringite,	Fibrous,	$Mg,[Al_2]^{VIII}O_8^{VIII}(SO_2)_4 \cdot 22\,H_2O$
Apjohnite,	Fibrous,	$Mn,[Al_2]^{VIII}O_8^{VIII}(SO_2)_4 \cdot 22\,H_2O$
Halotrichite,	Fibrous,	$Fe,[Al_2]^{VIII}O_8^{VIII}(SO_2)_4 \cdot 22\,H_2O$

Phosphates.

Lazulite,	Monoclinic,	$H_2,Mg,[Al_2]^{X}O_{10}^{X}P_2$
Turquois,	Reniform,	$O_8^{\equiv}[Al_2]_2^{\equiv}O_6^{\equiv}(PO)_2$
Wavellite,	Orthorhombic,	$[Al_2]_3^{XVIII}O_{18}^{XVIII}(PO)_4,H_6 \cdot 5\,H_2O$

Silicates.

Andalusite, Cyanite,	Orthorhombic, Monoclinic,	$O=[Al_2]^{\equiv}O_4^{\equiv}Si$
Topaz,	Orthorhombic,	$F_2=[Al_2]^{\equiv}O_4^{\equiv}Si$

Feldspars.

Anorthite,	Triclinic,	$Ca,[Al_2]^{VIII}O_8^{VIII}Si_2$
Labradorite,	Triclinic,	$[Na_2Ca],[Al_2]^{VIII}O_8^{VIII}Si_3O_2$
Leucite,	Isometric,	$K_2,[Al_2]^{VIII}O_8^{VIII}Si_4O_4$
Oligoclase,	Triclinic,	$[Ca,Na_2],[Al_2]^{VIII}O_8^{VIII}Si_5O_6$
Albite,	Triclinic,	$Na_2,[Al_2]^{VIII}O_8^{VIII}Si_6O_8$
Orthoclase,	Monoclinic	$K_2,[Al_2]^{VIII}O_8^{VIII}Si_6O_8$

Clays.

Kaolinite,	Orthorhombic,	$H_2,[Al_2]^{VIII}O_8^{VIII}Si_2 \cdot H_2O$
Halloysite,	Massive,	$H_2,[Al_2]^{VIII}O_8^{VIII}Si_2 \cdot 2\,H_2O$
Pyrophyllite,	Orthorhombic,	$H_2,[Al_2]^{VIII}O_8^{VIII}Si_3O_2$
Agalmatolite,	Massive,	$H_2,[Al_2]^{VIII}O_8^{VIII}Si_4O_4$

Zeolites.

Thomsonite,	Orthorhombic,	$[Na_2,Ca],[Al_2]^{VIII}O_8^{VIII}Si_2 \cdot 2\frac{1}{2}\,H_2O$
Natrolite,	Orthorhombic,	$Na_2,[Al_2]^{VIII}O_8^{VIII}Si_3O_2 \cdot 2\,H_2O$
Scolecite,	Monoclinic,	$Ca,[Al_2]^{VIII}O_8^{VIII}Si_3O_2 \cdot 3\,H_2O$
Analcime,	Isometric,	$Na_2,[Al_2]^{VIII}O_8^{VIII}Si_4O_4 \cdot 2\,H_2O$
Chabazite,	Hexagonal,	$Ca,[Al_2]^{VIII}O_8^{VIII}Si_4O_4 \cdot 6\,H_2O$
Harmotome,	Orthorhombic	$Ba,[Al_2]^{VIII}O_8^{VIII}Si_5O_6 \cdot 5\,H_2O$
Heulandite,	Monoclinic,	$Ca,[Al_2]^{VIII}O_8^{VIII}Si_6O_8 \cdot 5\,H_2O$
Stilbite,	Orthorhombic	$Ca,[Al_2]^{VIII}O_8^{VIII}Si_6O_8 \cdot 6\,H_2O$

To this list may be added the *Garnets*, the *Scapolites*, the *Epidotes*, the *Micas*, and the *Chlorites*, all large and important groups of minerals, which are chiefly silicates of aluminum, but which present differences of composition similar to those illustrated above. It is impossible, however, in the present state of the science, to deduce from the results of the analysis of many of these minerals any satisfactory or probable rational formula. The mineral Lapis Lazuli is a remarkable illustration of this fact. It has a definite crystalline form (Fig. 2), and has long been used as a paint under the name of Ultramarine. It is a silicate of aluminum, calcium, and sodium, with a sulphide probably of iron and sodium; but numerous analyses have given no definite clew either to its rational formula or to the cause of its beautiful blue color. Nevertheless, the pigment is now made artificially in large quantities, by combining the ingredients in the proportions which the analyses have indicated, and this would seem to show that it is the theory, and not the analysis, which is at fault. This subject will be further discussed under Silicon.

It will be noticed that among the native compounds of aluminum are included several of the precious stones, and also Emery, which yields an exceedingly hard powder very much used in polishing. From the clays, the clay slates, and to a less extent from the rarer minerals Alum-stone and Beauxite, the alums and other soluble salts of aluminum are prepared. Cryolite, now imported from Greenland in large quantities, has become an important source of soda-ash. The feldspars, and more immediately the clays which result from their disintegration, are largely used in the manufacture of porcelain and the various kinds of earthen-ware. The coarser clays furnish the material for bricks. The slates, the porphyries, the granites, the trachytes, the greenstones, the lavas, and similar rocks rich in aluminum, are used in building; but the other aluminous minerals, with few exceptions, find no important applications in the arts.

284. **Metallic Aluminum.** — Readily obtained by reducing either the chloride or the native fluoride (Cryolite) with metallic sodium. It has a brilliant white lustre, and possesses to a high degree all the qualities of a useful metal. It has a low specific gravity (2.56), but still a very great tenacity. It is singularly sonorous. It is very malleable and ductile. It is an excellent conductor of heat and electricity. It has a high melting point, although somewhat lower than that of silver. It does not tarnish in the air, and the molten metal does not oxidize

even when heated to a high temperature. Its present cost, which depends solely on the difficulty of extraction, greatly restricts the application of aluminum in the arts; but nevertheless it is used to a limited extent for cheap jewelry, and in a few philosophical instruments, where it is important to combine lightness with strength. An alloy of copper with about ten per cent of pure aluminum, called Aluminum Bronze, has the color of gold, and an almost equal power of resisting atmospheric agents.

Neither sulphuric nor nitric acid, when cold and sufficiently diluted, attacks aluminum, and nitric acid dissolves it only slowly when concentrated and boiling. Hot sulphuric acid, however, when not diluted with more than three or four parts of water, dissolves it rapidly, with the evolution of hydrogen gas. The best *acid* solvent is hydrochloric acid, which acts on the metal at the ordinary temperature even when greatly diluted; but, singularly, the metal dissolves almost equally well in a solution of caustic soda or potash; and a comparison of the two following reactions will make evident one of the most important features in the chemical relations of this metal.

$$Al{=}Al + (6\ H\text{-}Cl + Aq) = ([Al\text{-}Al]{\equiv}Cl_6 + Aq) + 3\ H\text{-}H. \quad [238]$$

$$Al{=}Al + (6\ Na\text{-}O\text{-}H + Aq) = (Na_6{\equiv}O_6{\equiv}[Al\text{-}Al] + Aq) + 3\ H\text{-}H. \quad [239]$$

285. **Compounds in which $[Al_2]$ is the Basic Radical.** — The compounds of this class are isomorphous with, and resemble in almost every respect, excepting color, the corresponding ferric salts. Like the last, they have a great tendency to form basic salts, and they exhibit in general the same reactions which have been already described (§ 268). The use of the soluble aluminic salts in the arts depends, — 1st. Upon their tendency to form insoluble basic compounds; and 2d. Upon the fact that these basic compounds, including the hydrates, eagerly absorb the soluble organic extracts used as dyes. When organic tissues, yarn or cloth, are dipped into a solution of a basic aluminic salt (compare note to page 388), or when in the process of calico printing a similar preparation is transferred to the surface of the fabric in regular designs, the insoluble basic compounds just referred to are formed in the very fibre of the material, and become still more firmly incorporated when the tissue is exposed to the action of air, steam, or other agents, in the process known as *aging*. If now the yarn or cloth thus prepared is dipped in a dye-vat, the aluminic compound entangled in the fibre will seize and hold the coloring matter, and hence the

name of mordants, from *mordeo* (*to take fast hold of*), applied to these preparations of aluminum. The basic ferric, chromic, and stannic salts act in a similar way, and are also used as mordants; but while the colorless aluminic salts take the true color of the dye, the others modify the tint to a greater or less extent. Hence, in the process of calico-printing, various colors are obtained from the same bath, after the design has been printed on the cloth with the appropriate mordants. When salts of aluminum are mixed in solution with dyestuffs, and decomposed by an alkaline reagent, the insoluble hydrate or basic salt thus formed carries down a large amount of the coloring matter, and these colored precipitates, when dried, are used as pigments (*Lakes*).

Of the soluble salts of aluminum which may be used as mordants, the most important are the alums, whose symbols have already been given (§ 283). They alone crystallize readily, and can therefore be easily manufactured on a large scale in a condition which insures purity. The alkaline sulphate which they contain, although it determines the peculiar crystalline character of these double salts, is wholly worthless to the dyer, and it depends chiefly on the ruling price whether the ammonic or the potassic salt is employed in their manufacture. Sodic alum does not crystallize readily, and is therefore never used. The aluminic sulphate, which is the only useful part of the alum, is generally obtained by decomposing clay or shale, after it has been roasted at a low red heat with sulphuric acid. It is made in large quantities in England and Germany from a bituminous shale, found among the lowest beds of the coal measures, which contains a large quantity of iron pyrites disseminated through the mass. When this alum schist, or alum ore as it is called, is slowly burnt, one half of the sulphur of the pyrites is converted into sulphuric acid, which at once decomposes a portion of the aluminic silicate that the shale contains, thus yielding a certain amount of aluminic sulphate. At the same time ferrous sulphate is formed by the oxidation of the residue of the pyrites, and when the roasted mass is lixiviated with water both salts dissolve. Lastly, on adding to the solution, after concentration, potassic or ammonic sulphate, alum is formed, which is separated from the ferrous salt by crystallization.

A small amount of potassium alum is made in the Roman States from Alum-stone (§ 283). This mineral, when roasted and exposed for several months to the action of air and moisture, crumbles into a

sort of mud, which, when lixiviated, yields the well-known Roman alum.

Within the last few years the use of alum has been in a measure superseded by the introduction into commerce of pure aluminic sulphate, which is made by the direct action of sulphuric acid on some of the purer varieties of clay, and freed from iron by means of sodic ferrocyanide. This reagent is added to the solution so long as it occasions a blue precipitate, and after this settles the clear liquid is decanted and evaporated. The residue is known as *concentrated alum*. The salt may be crystallized in small scales, which have the composition given below.

A solution of basic aluminic acetate is also much used as a mordant, especially for madder-reds, under the name of Red Liquor. It is prepared by adding plumbic acetate to a solution of alum. The only important soluble salts of aluminum which have not yet been mentioned are the chloride and nitrate.

Aluminic Chloride,	$[Al_2]\equiv Cl_6 \,.\, 12\, H_2O$
Aluminic Nitrate,	$[Al_2]\equiv O_6\equiv (NO_2)_6 \,.\, 18\, H_2O$
Aluminic Sulphate,	$[Al_2]\equiv O_6\equiv (SO_2)_3 \,.\, 18\, H_2O$

The reactions of the aluminic salts, when in solution, differ from those of the corresponding ferric salts chiefly in the fact that the white aluminic hydrate, which is precipitated by the alkaline reagents, dissolves easily and perfectly in an excess of either potassic or sodic hydrate. A compound of aluminum may generally be recognized by the blue color which is obtained when the solid, previously moistened with a solution of cobaltic nitrate, is intensely heated in the oxidizing flame of the blowpipe.

286. **Compounds in which $[Al_2]$ is the Acid Radical.** — Sodic aluminate, the same compound which is formed by [239], is now manufactured on a large scale from Beauxite. The pulverized mineral, mixed with sodic carbonate, is heated to bright redness, and the soluble aluminate thus formed separated from the insoluble residue by lixiviation and filtration. On evaporating the clear solution (*in vacuo*), a white amorphous solid is obtained, which has the composition already given. Aluminic hydrate is precipitated from solutions of this compound on the addition of any soluble acid, or even on exposure to the carbonic acid of the atmosphere, and this new commercial product may be used with great advantage as a substitute for alum. A remarkable

reaction occurs when solutions of aluminic chloride and sodic aluminate are mixed together in atomic proportions, illustrating the singular twofold relations which the radical $[Al_2]$ may sustain.

$$([Al_2]\equiv Cl_6 + Na_6\equiv O_6\equiv[Al_2] + 6\,H_2O + Aq) = 2\,[Al_2]\equiv O_6\equiv H_6 + (6\,NaCl + Aq). \quad [240]$$

Although other aluminates may be prepared, the salt just described is the only noteworthy example of this class of compounds. Spinel, however, and the allied minerals, may be regarded as meta-aluminates.

287. **Aluminic Chloride**, $[Al_2]\equiv Cl_6$, is the only compound of aluminum with chlorine. It is made by passing chlorine gas into a mixture of aluminic oxide with carbon, heated intensely in an earthern retort, when the chloride distils over and condenses in the receiver in yellowish-white crystalline scales. It is a fusible solid, which volatilizes at a temperature only a few degrees above its melting point, and the Sp. Gr. of its vapor confirms the theory of its constitution generally accepted. It eagerly unites with water, but, like ferric chloride, it cannot be recovered by evaporation when once dissolved. It forms double salts with the alkaline chlorides, and one of these, $[Al_2]\equiv Cl_6 . 2\,NaCl$, plays an important part in the preparation of aluminum.

Not only Al_2Cl_6, but also Fe_2Cl_6, when anhydrous, determine certain very remarkable reactions between the hydrocarbons of the aromatic series and the chlorine or bromine compounds of various hydrocarbon radicals. The effect is to set free HCl or HBr, and to replace one or more of the hydrogen atoms of the hydrocarbon with the radical in question, thus:—

$$(C_6H_6 + C_2H_5Cl + xAl_2Cl_6) = (C_6H_5\text{-}C_2H_5 + xAl_2Cl_6) + HCl. \quad [241]$$

The Al_2Cl_6 which appears to act as the medium of the reaction remains unchanged, and the theory of the process is still obscure.

288. **Aluminic Oxide**, Al_2O_3, forms, as we have seen, the mineral Corundum. It may be obtained artificially by igniting either ammonium alum, or the hydrate obtained indirectly from Beauxite (§ 286). It is a hygroscopic white powder, which adheres to the tongue, but does not become plastic when mixed with water. It affects, like ferric oxide, two conditions, and the change from one to the other is accompanied in like manner by a sudden incandescence. It may be fused by the compound blowpipe, and the resulting transparent bead, like Corundum, has a hardness only inferior to that of Diamond. Mor-

over, colored crystals resembling the Ruby and the Sapphire have been obtained by art.

289. **Aluminic Sulphide,** $[Al_2]\overline{\overline{S}}_3$, is formed when finely divided aluminum is burnt in the vapor of sulphur. It is a black powder, which is rapidly decomposed by water into H_2S and $[Al_2]\overline{\overline{O}}_6\overline{\overline{H}}_6$. Hence H_2S does not under any conditions precipitate aluminum from solutions of its salts, and the precipitate obtained with the alkaline sulphides is simply the normal hydrate.

QUESTIONS AND PROBLEMS.

1. Why is not the atomic weight of aluminum doubled according to the principle of § 20?

2. Can the composition of the native fluorides of aluminum be expressed by unitary symbols (§ 54)? Can you devise a process by which sodic carbonate may be made from Cryolite?

3. Compare together the minerals isomorphous with Spinel (§§ 283, 264, 273), and show in what two ways their constitution may be expressed.

4. Compare the crystalline form and hardness of Corundum with those of the allied sesquioxides.

5. Compare the native aluminic with the native ferric hydrates, and show how many of the possible hydrates are represented among the native aluminic salts. Use the table of ferric hydrates already made (Prob. 67, Div. XIV.).

6. Make a table of the known compounds of the two alum types.

7. What inference should you draw from a comparison of the symbols of the different aluminum compounds as regards the isomorphism of calcium with the alkaline radicals?

8. Some varieties of Pyrophyllite closely resemble Steatite. By what simple blowpipe test can the two minerals be distinguished?

9. Write the reaction of sodium on sodio-aluminic chloride or fluoride, and calculate how much aluminum can be obtained theoretically for every kilogramme of sodium employed.

10. How does the *Sp. Gr.* of aluminum compare with that of the other useful metals?

11. Write the reaction of nitric acid and that of sulphuric acid on aluminum, assuming that nitric oxide is evolved in the first case, and hydrogen gas in the second.

12. Compare reactions [238] and [239], and point out the different relations of the radical $[Al_2]$ in the two cases.

13. Explain the peculiar relations of the aluminic salts on which their use as mordants depends.

14. Write the reaction which takes place when sodic carbonate is added to a solution of alum, so long as the precipitate first formed is redissolved, assuming that the basic aluminic sulphate which remains in solution contains one "atom" SO_2 to each atom Al_2.

15. What are the relative intrinsic values of potassium alum, ammonium alum, and crystallized aluminic sulphate, taking as the standard the quantity of normal aluminic hydrate which can be obtained from each? On what does the preference given to the alums as mordants chiefly rest?

16. Explain and illustrate by reactions the process of manufacturing alum from the alum shales, and also from pure clay.

17. Illustrate by reactions the change of Alum-stone into alum in the manufacture of Roman alum.

18. If a portion of the water obtained in the analyses of Aluminite and Paraluminite is water of constitution, how may the symbols be written?

19. Write the reaction of plumbic acetate on a solution of alum, assuming that the basic acetate, which remains in solution, contains one atom Al_2 to every three atoms C_2H_3O.

20. What are the two chief differences between the chemical relations of iron and aluminum? Illustrate the differences by reactions.

21. Explain and illustrate by reactions the method of manufacturing sodic aluminate. By what test could you determine when all the soda has been converted into sodic aluminate? Why evaporate solution *in vacuo*?

22. Write reaction of CO_2 on solution of sodic aluminate, and explain the use of this salt as a mordant.

23. Analyze reaction [240].

24. Show how Spinel could be derived from a tetrahydro-magnesic aluminate.

25. Write the reaction by which aluminic chloride is formed, and show that the Sp. Gr. of its vapor confirms the theory of its constitution generally accepted.

26. Write the reaction which takes place when a solution of aluminic chloride is evaporated to dryness. Consider whether the product formed by the union of the anhydrous chloride with water ought to be regarded as a chemical compound, and, if so, endeavor to represent its constitution by a rational symbol.

27. Compare the reactions of ammonic sulphide on an aluminic and on a ferric salt, and explain the cause of the difference.

28. In what order would you classify the several radicals $[R_2]$, regarding their electro-negative relations?

DIVISION XVII.

290. **GLUCINUM.** $Gl = 13.9$. — $[Gl_2]$ is probably sextivalent, like $[Al_2]$. A metallic element found in Beryl, $Gl_2^{VI}O_6^{VI}(Si_6O_6)^{VI}O_6^{VI}Al_2$, Chrysoberyl, $Gl_2O_3 \cdot 3\,Al_2O_3$, and a few other rare minerals. The metal is very light (*Sp. Gr.* 2.1), is malleable, has a bright white lustre, does not alter in the air even when heated, and does not decompose aqueous vapor at a red heat. It resembles aluminum, as do also its oxide, hydrate, and chloride, the corresponding compounds of the same element. The hydrate differs from that of aluminum, however, in several important respects. Although soluble in caustic alkalies, it is again precipitated on boiling the diluted solution. It dissolves in solutions of ammonic carbonate, with which it forms a crystalline salt. It yields with sulphuric acid a well-crystallized sulphate, $Gl_2O_6(SO_2)_3 \cdot 12\,H_2O$, which forms with potassic sulphate a double salt, $K_6, Gl_2^{VI}(SO_4)_6 \cdot 6\,H_2O$, wholly different from alum. Lastly, it absorbs CO_2 from the air. The salts of this metal have an acid reaction and a sweet taste, whence the name, from γλυκύς. The European chemists, however, usually name the metal Beryllium, and write the symbol *Be*. There is still a question in regard to the quantivalence of this element. Some chemists regard the oxide as of the type RO allied to MgO, and if so, the atomic weight of the element would be 9.3; but a recent determination of the specific heat of glucinum, giving the value 0.4084, favors the theory here adopted, that glucina is a sesquioxide, and this view is supported by the fact that glucina replaces alumina in the mineral Danalite. The classification of Mendelejeff assumes that $\overset{II}{Gl} = 9.3$, and hence the question in regard to the molecular structure and affinities of the oxide is one of great importance.

291. **GALLIUM.** $Ga = 69.8$. — This metal was discovered by means of the spectroscope in a zinc Blende from the Pyrenees, and has since been found in very minute quantities in blendes from a few other localities. The 62 grammes of Gallium exhibited in the Paris Exposition of 1878 were prepared from 2,400 kilogrammes of this mineral. The metal is bluish white, and has the remarkable property of fusing at 30°.1. The molten metal resembles mercury, and remains liquid for several weeks even at 0°. If, however, the globule is touched with a small fragment of the solid metal, it at once crystallizes. But

although so fusible, gallium is not volatile at a red heat, and only a thin film of oxide forms on the surface. The *Sp. Gr.* of the metal is 5.9, and the specific heat 0.080. It readily dissolves in dilute hydrochloric acid, and also in solution of caustic alkali, with evolution of hydrogen. The oxide, Ga_2O_3, is a white powder, insoluble in water, but readily soluble in potash and in ammonia. The chloride, Ga_2Cl_6, is very deliquescent, but the aqueous solution when diluted becomes turbid, owing to the formation of an insoluble basic salt. The sulphate combines with ammonic sulphate to form a double salt having the same constitution and crystalline form as alum.

292. **INDIUM.** $In = 113.4$. — This metal is another associate of zinc found in the zinc blende of Freiberg and of a few other localities, and, like gallium, was discovered with the spectroscope. It takes its name from a well-marked indigo-blue band which its flame shows when examined with this instrument. Although less volatile than zinc, it comes over in the process of distillation (§ 226) with the great mass of the metal with which it remains alloyed, and the zinc of Freiberg contains about one tenth of one per cent of indium. The metal is softer than lead. *Sp. Gr.* 7.42. Melting point, 176°. It has a white metallic lustre, which it retains in the air, and does not act on boiling water. The best solvent is nitric acid, but it dissolves slowly in hydrochloric and dilute sulphuric acids. Heated on charcoal before the blowpipe it colors the flame blue, and gives an incrustation of the oxide. This oxide, In_2O_3, is a pale yellow powder, which becomes brown on heating. The hydrate, In_2Ho_6, formed when ammonia is added to a solution of an indium salt, is a gelatinous precipitate, which becomes more dense on boiling, and readily changes into the oxide.

Indium chloride, In_2Cl_6, is an extremely deliquescent white solid which dissolves in water with a hissing noise and evolution of heat. On evaporating the solution, a basic salt is obtained. Indium sulphate combines with the alkaline sulphates and forms well-defined crystals having the form and constitution of alum.

DIVISION XVIII.

293. **YTTRIUM, ERBIUM, and their Associates.** — The rare minerals Gadolinite, Euxenite, Keilhauite, and Samarskite contain a mixture of earths which quite closely resemble glucina. In general, however, they differ from it in forming insoluble oxalates, and hence are precipitated on adding an excess of oxalic acid to solutions of their salts. Their hydrates also are insoluble in caustic soda or potash, although they dissolve readily in solutions of ammonia and its carbonate. By different processes of fractional treatment there have been separated from this mixture of earths a number of metallic oxides whose molecular weights vary from about 61 to 147, and the metallic radicals of these earths have been called by different chemists Scandium, Yttrium, Ytterbium, Terbium, Decipium, Holmium, Thulium, Erbium, etc. For the most part, at least, these oxides are distinguished by no well-marked characters except the varying molecular weight and the position of the bands which they give in the spectroscope; characters which present such complications that it is difficult to interpret them. Hence, although there evidently exist in this mixture of earths a number of separate elements, yet it is impossible to say how many, or how far the distinctions claimed by the authors of the above names are valid. Moreover, we cannot at present decide whether these oxides are protoxides or sesquioxides, although the probability favors the latter view, at least in regard to most of them. The spectroscopic characters are by far the most distinctive features of these substances, and one or more of them present very striking phenomena of this class. The substance formerly called Erbium Oxide shines with a green light, although it does not apparently volatilize, and with the spectroscope the unique phenomenon is seen of brilliant colored bands superimposed on a continuous spectrum. Moreover, solutions of the salts of this earth absorb the same colored rays which the ignited oxide emits; and when a luminous flame is viewed with a spectroscope through such a solution, dark bands are seen, which have the same position as the luminous bands just mentioned. The student will, of course, understand that the opinions here expressed are based on the knowledge in regard to these earths which has thus far been published. Several able chemists are at present investigating the subject, and we may soon expect more definite results.

DIVISION XIX.

294. **CERIUM**, $Ce = 141$, **LANTHANUM**, $La = 139$, **and DIDYMIUM**, $D = 140$?— These three rare elements are found inseparably united in Cerite, Allanite, Lanthanite, Yttrocerite, Parasite, and several other very rare minerals. They are not unfrequently associated with the elements of the last section, which they resemble in many particulars, but they differ from them in forming with potassium insoluble double sulphates, and hence they are precipitated on adding an excess of potassic sulphate to solutions of their salts. They all yield oxides of the form R_2O_3, but cerium differs from the other two in forming a higher oxide, probably CeO_2, which, when heated with hydrochloric acid, evolves chlorine. The oxides of cerium and lanthanum are more or less colored, and that of didymium is dark brown. The salts of didymium are pink or violet-colored, and when in solution, even in small quantities, absorb powerfully certain rays of light; and the spectrum of a luminous flame viewed through such a solution shows a strong absorption band in the yellow and another in the green. As these bands differ wholly from those of the erbium earths, they enable us to recognize with certainty the presence of didymium, as none of its associated elements produce any such effect. Moreover, since the characteristic absorption bands are seen with reflected as well as with transmitted light, we are enabled to extend this mode of investigation even to opaque solids.

In regard to the elementary substances but little is known. Cerium, which has been obtained by reducing its chloride with sodium, is a soft metal like lead. When polished, it exhibits a high metallic lustre, and its specific gravity is about 5.5.

QUESTIONS AND PROBLEMS.

1. Some chemists regard glucina as a protoxide like magnesia, and hence write the symbol *GlO*. What would then be the atomic weight of glucinum? Ans. 9.3.

2. What would be the symbols of Beryl and Chrysoberyl on the assumption of the last problem?

3. If the yttrium and erbium earths present such marked spectroscopic characters, why is there so much difficulty in defining the separate elements?

Consider also why the great differences of molecular weight give us no certain means of distinction. Consider also what bearing the existence of a series of oxides with molecular weights varying between such extremes must have on the principle of the classification of Mendelejeff. Compare with this fact the closely agreeing atomic weights of nickel, cobalt, manganese, iron, and chromium.

4. By what two reagents may the elements of this section be divided into three groups? Ans. Oxalic acid and potassic sulphate.

5. When mixed with the other allied oxides, the amount of ceric oxide present may be determined by dissolving, out of contact with the air, a weighed amount of the mixed oxides in hydrochloric acid, to which some potassic iodide has been added, and then finding by [158] the quantity of iodine thus set free. Write the reactions illustrating the theory of the process. Ans. in part. $Ce_4O_4 + 8HCl = 3CeCl_2 + 4H_2O + Cl_2$

DIVISION XX.

295. **GOLD.** $Au = 197$. — Trivalent. Almost always found in the native state, or only slightly alloyed with other metals. The only well-defined native compounds are those with tellurium. Very sparingly but very widely disseminated through many of the cystalline rocks and in the alluvium resulting from their disintegration. In the gold-bearing rocks the metal is frequently found accumulated to a greater or less extent in veins of Quartz (Auriferous Quartz). It is also constantly associated in minute quantities with other metallic ores, especially with those of silver, and in some localities the veins of iron and copper pyrites yield large amounts of the precious metal. It is extracted either by simple washing, or by bringing the finely pulverized ore in contact with metallic mercury, which has a great affinity for gold, and picks out the minute particles from the mass of refuse. The process is very simple, and the cost of the product depends, to a great extent, on the very large amount of material which must be handled; for gold ores contain on the average but a few ounces of metal to the ton. From the resulting amalgam the mercury is recovered by distillation, and the residual metal may then be melted and cast into bars. The gold thus obtained, however, is more or less alloyed, chiefly with silver, and is refined before being used for coinage. This is best accomplished by dissolving the metal in aqua-regia, evaporating to dryness to remove the excess of nitric acid, dissolving in a large volume of water, and precipitating the gold with ferrous sulphate. Lastly, the precipitate is collected and melted under borax. If the proportion of alloy is very large, it is best removed by boiling the metal with nitric or sulphuric acid. When nitric acid is used for parting gold from silver, the separation is not complete when the amount of gold is more than one fourth of the weight of the alloy; and since in most cases the alloy must be first reduced to this proportion, the process is called *quartation*. When sulphuric acid is used, the amount of gold must not exceed one fifth.

Gold has been called the king of metals; for it not only possesses the qualities distinguishing a metal in their highest perfection, but also, under all ordinary conditions, preserves its brilliant lustre unimpaired. With the exception of platinum, iridium, and osmium, gold is the densest solid known; *Sp. Gr.* 19.34. It may be drawn into wire

of such fineness that three kilometres weigh only a single gramme, and may be beaten into leaves not more than one ten-thousandth of a millimetre thick. Gold has a familiar yellow color, but thin leaves transmit a green light. It has been found that an exceedingly thin film of gold attached to the surface of a glass plate, and heated to a temperature not exceeding 315°, loses its metallic lustre and appears ruby-red by transmitted light; and finely divided gold, when suspended in water or melted into glass, imparts to the medium the same beautiful color. Gold is nearly as soft as lead, and pieces of pure gold may be welded together without heat by pressure or concussion, as in dentistry. In order to increase its hardness it is alloyed with copper. The standard gold of both the United States and the French coinage contains one tenth copper, that of the English one twelfth of the same alloy. Gold melts at about 1,100°. It is only slightly volatile at the highest furnace heat; but before the compound blowpipe it is dispersed in purple vapor. It is an excellent conductor of heat and electricity, but is inferior in this respect both to silver and copper.

Gold is not dissolved by any of the common acids, and is not attacked by the fused caustic alkalies. It enters, however, into direct union both with chlorine and bromine, and is readily dissolved by any liquid mixture which liberates chlorine. The usual solvent is a mixture of four parts of hydrochloric acid with one of nitric acid, called, on account of its power of dissolving gold, aqua-regia.

$$Au + Au + (2\,HNO_3 + 6\,HCl + Aq) = (2\,AuCl_3 + 4\,H_2O + Aq) + 2\,NO. \quad [242]$$

When gold is dissolved in aqua-regia, if hydrochloric acid is used in excess, the solution, evaporated at a gentle heat, yields *yellow* needle-shaped crystals, which appear to be a molecular compound of $AuCl_3$ with HCl. If, however, the evaporation is pushed still further, but at a temperature not exceeding 120°, a *red* crystalline mass is obtained, which is essentially *Auric Chloride*, $AuCl_3$, although it is difficult to expel the last traces of HCl without still further decomposing the salt. If this product is heated above 160° it loses two atoms of chlorine, and there is left a pale yellow sparingly soluble powder, which is *Aurous Chloride*, $AuCl$, and at 200° this last is also decomposed and reduced to metallic gold. Auric chloride is deliquescent, and yields an orange-colored solution easily distinguished from the solution of $AuCl_3 . HCl$, which is yellow. It also forms yellow crystalline salts with the alka-

line chlorides, similar in constitution to the compounds with *HCL*. Their formulas are $AuCl_2 . KCl . 5 H_2O$, and $AuCl_3 . NaCl . 4 H_2O$. In like manner it unites with ammonic chloride and with the chlorides of most of the organic bases, forming crystallizable salts, which are often employed to determine the molecular weight of these alkaloids. Auric chloride is a very unstable compound, and is readily reduced to the metallic state. Solutions of ferrous sulphate, of antimonious chloride, of oxalic acid, and of sulphurous acid, all precipitate the gold in a finely divided state. Phosphorous and hypophosphorous acid and solutions of their salts produce the same effect, as do also phosphorus itself and many of the metals. The brown gold powder thus obtained is much used for gilding porcelain. A solution of stannous chloride mixed with stannic chloride produces in neutral solutions of auric chloride a beautiful purple precipitate called Purple of Cassius, which is much used for coloring glass and porcelain. The compound contains both gold and tin combined with oxygen, but its chemical constitution is still in question. Metallic tin gives a similar precipitate. There appear to be two iodides of gold, *AuI* and AuI_3, but only one bromide, $AuBr_3$, has been described. There are also two oxides, Au_2O_3 and Au_2O. The first acts as an acid, the second as a very feeble basic anhydride. The following reactions illustrate the formation and relations of these compounds.

$$(AuCl_3 + 6\,K\text{-}O\text{-}H + Aq) = (K_3^{\equiv}O_3^{\equiv}Au + 3\,KCl + 3\,H_2O + Aq). \quad [243]$$

$$K_3^{\equiv}O_3^{\equiv}Au + 3\,H\text{-}O\text{-}C_2H_3O + Aq) = H_3^{\equiv}O_3^{\equiv}Au + (3\,K\text{-}O\text{-}C_2H_3O + Aq). \quad [244]$$

$$2\,H_3^{\equiv}O_3^{\equiv}Au = Au_2O_3 + 3\,H_2O. \quad [245]$$

To obtain these reactions, the solution of $AuCl_3$ should be boiled after the addition of *K-O-H*, and then acidified with acetic acid. The precipitate thus obtained has, when dried, the composition of Au_2O_3. The compound Au_2O is obtained as an insoluble violet powder by digesting *AuCl* with a solution of caustic alkali.

$$(2\,AuCl + 2\,Na\text{-}O\text{-}H + Aq) = Au_2O + (2\,NaCl + H_2O + Aq). \quad [246]$$

It does not enter into direct combination with acids, but there is a thiosulphite of gold and sodium which plays an important part in photography, and appears to have the formula $Au,Na_3^{\equiv}O_4^{\equiv}(S\text{-}O\text{-}S)_2$. Singularly, however, gold is not precipitated from the solution of this

[illegible] by the ordinary reagents. There are two sulphides of gold, Au_2S and Au_2S_3. The first is precipitated by H_2S from a cold solution and the last from a boiling solution of $AuCl_3$ by the same reagent. They both dissolve in alkaline sulphides and form sulpho-salts. Thus,

$$Au_2S_3 + [(NH_4)_2S + 3H_2O] = [2NH_4(AuS_2) + 4H_2O] + 2H_2S. \quad [347]$$

[illegible] — With the exception just noted, gold, when in solution, can be distinguished by the fact that it is precipitated by ferrous sulphate, provided the solution, though acid, do not contain an excess of nitric acid.

$$(2AuCl_3 + 6FeCl_2) + Aq = Au + (2FeCl_3 + 4FeCl_3) + Aq. \quad [348]$$

The formation of Purple of Cassius, and the easy reduction of all its compounds to the metallic state by simple ignition, are other indications by which the presence of gold may be readily recognized. The polished gold, even when in fine powder, acquires its peculiar lustre if rubbed against a hard surface, as in the process of burnishing. Besides the important uses of gold for coinage and for articles of ornament or luxury, the metal is peculiarly well adapted, both by its softness and its power of resisting corrosive agents, for its applications in dentistry. It is also largely employed in the various methods of gilding, which consist either in directly applying thin gold-leaf to the surface to be covered, or, when the surface is metallic, by depositing upon it a thin film of gold with the aid of galvanism or by the simple action of chemical affinity.

QUESTIONS AND PROBLEMS.

1. *Write the reactions of sulphurous acid and of oxalic acid on solution of auric chloride, assuming that sulphuric acid in one case, and CO_2 in the other, are a part of the products.*

2. *What evidence do you find of the quantivalence of gold in the above sections?*

3. *Does gold act as an acid or a basic radical?*

4. *What is the chief chemical characteristic of gold?*

5. *There has been a question about the cause of the color which Purple of Cassius imparts to glass and porcelain glaze. Do the facts stated above explain this phenomenon?*

DIVISION XXI.

297. **BORON.** $B = 11$. — Trivalent. Very sparingly distributed. Always found in combination with oxygen. In boric acid and in various borates, including the minerals Datholite and Danburite, boron is the electro-negative element, while in Axinite and Tourmaline, and in many artificial salts, it acts the part of a basic radical. The elementary substance may be obtained both in an amorphous and a crystalline form. The first is obtained by decomposing boric anhydride with sodium.

$$B_2O_3 + 3\,Na{-}Na = 3\,Na_2O + B_2. \qquad [249]$$

It is an infusible dark brown powder, which soils the fingers and dissolves slightly in water. At about 300° it takes fire in the air and burns into B_2O_3, and it is also oxidized when heated with sulphuric acid or with the alkaline nitrates, sulphates, carbonates, or hydrates. It decomposes nitric acid even when slightly concentrated and cold.

$$B_2 + 3\,H_2{=}O_2{=}SO_2 = B_2O_3 + 3\,H_2O + 3\,SO_2. \qquad [250]$$

$$B{\equiv}B + 6\,KNO_3 = 2\,K_3{\equiv}O_3{\equiv}B + 6\,NO_2. \qquad [251]$$

Boron is one of the very few elements which unite directly with nitrogen.

$$B_2 + N{\equiv}N = 2\,BN. \qquad [252]$$

If amorphous boron is heated intensely in a closed crucible, it becomes much denser, and is then less easily oxidized. It dissolves in melted aluminum, and when the molten metal sets, the boron crystallizes in square octahedrons (§ 106) more or less highly modified. These crystals are nearly as hard as the diamond, have an adamantine lustre, and *Sp. Gr.* = 2.68. They may also be obtained directly from boric anhydride, which is decomposed by aluminum.

$$[Al_2] + B_2O_3 = [Al_2]O_3 + B_2 \qquad [253]$$

The crystals thus prepared are sometimes nearly colorless, but more frequently they have a yellow or red color, and sometimes the color is so deep that they appear black. They are probably never wholly pure, and it is worthy of remark that they sometimes, if not always, contain a considerable quantity of carbon. They resist the action of

all acids, and even of fused nitre, but are oxidized when fused with acid potassic sulphate. It appears, from recent investigations, that the so-called graphitoidal boron, which is formed with the crystals just mentioned, is a compound of aluminum and boron.

298. **Boric Acid.** $H_3{=}O_3{=}B$. — A product of volcanic action. Found in some natural waters, and has been detected in the waters of the ocean. It is collected in large quantities, but in an impure condition, from the hot vapors of the *fumerolles* in the Maremma of Tuscany. The pure acid is best prepared from borax by the reaction

$$(Na_2{=}O_2{=}B_4O_5 + 2\,HCl + 5\,H_2O + Aq) = 4\,H_3{=}O_3{=}B + (2\,NaCl + Aq). \quad [254]$$

The hydrochloric acid should be mixed with a hot saturated solution of borax, which as it cools deposits boric acid in white nacreous crystalline scales. Boric acid is sparingly soluble in cold water, but dissolves in three times its weight of boiling water. It is also soluble in alcohol, and imparts to the flame of burning alcohol a peculiar green tint, which exhibits in the spectroscope five well-marked green bands. Neither the aqueous nor the alcoholic solution can be evaporated without loss, as the vapor always takes with it an appreciable amount of the acid. The solution evaporated on turmeric paper changes the color to brown, like an alkali, but it affects litmus paper like other weak acids. At the temperature of 100° it loses one molecule of water.

$$H_3{=}O_3{=}B = H\text{-}O\text{-}BO + H_2O. \quad [255]$$

The compound $H_3{=}O_3{=}B$ is called orthoboric acid. The product $H\text{-}O\text{-}BO$ is frequently described as the first anhydride of this acid, and is called metaboric acid. If this is heated to a still higher temperature two molecules unite, while at the same time they lose another molecule of water, forming the second and last anhydride, boric anhydride.

$$2\,H\text{-}O\text{-}BO = B_2O_3 + H_2O. \quad [256]$$

At a red heat B_2O_3 fuses to a viscid glass, which remains clear as it cools, but soon becomes opaque and crumbles if exposed to the air. It also forms fusible compounds with the metallic oxides. Hence the use of boric acid and the borates as fluxes.

299. **Borates.** — It is evident from the principles of §§ 38 and 131, that, besides orthoboric acid, many others are theoretically possible. Thus: —

Boric Acid,	$H_3\equiv\overset{III}{O}_3\equiv B$
Diboric Acid,	$H_4\equiv O_4\equiv(B\text{-}\overset{IV}{O}\text{-}B)$
Triboric Acid,	$H_5\equiv O_5\equiv(B\text{-}O\text{-}B\text{-}\overset{V}{O}\text{-}B)$
Tetraboric Acid,	$H_6\equiv O_6\equiv(B\text{-}O\text{-}B\text{-}O\text{-}\overset{VI}{O}\text{-}B\text{-}O\text{-}B)$
Polyboric Acid,	$H_{n+2}O_{n+2}(B_n\overset{n+2}{O}_{n-1})$

These may be regarded as formed by the coalescing of several molecules of orthoboric acid, and the elimination from this condensed molecule of a sufficient number of molecules of water to set free the number of oxygen atoms required to cement together the atoms of boron in the resulting radical. By eliminating additional molecules of water, we may obtain from either of the above acids a series of anhydrides (distinguished as the first, second, etc. anhydrides), and the number of possible anhydrides in any case is equal to the number of pairs of hydrogen atoms which the acid contains. It must be understood that all these possible forms are not real compounds. Indeed, only the three already mentioned have been actually prepared; but there are several borates whose constitution is best explained when we regard them as salts of acids derived from orthoboric acid in the way just indicated. The most important of these is common borax, which may be regarded as the sodium salt of the second anhydride of tetraboric acid.

300. **Borax,** $Na_2\equiv O_2\equiv(B\equiv O_2\equiv B\text{-}\overset{II}{O}\text{-}B\equiv O_2\equiv B)\,.\,10\,H_2O$, was originally brought from a salt lake in Thibet, and was called Tincal. It also occurs in large crystals in the mud of Borax Lake, in California, and it has been found in solution in many mineral springs, and even in minute quantities in the ocean. Borax is manufactured in large quantities from the crude boric acid of the Tuscan lagoons. It is a white crystalline salt, which when heated gives up its water of crystallization, and at a red heat melts to a transparent glass, that has the property of dissolving almost all the metallic oxides. Many of the oxides impart to the glass characteristic colors; and these reactions, which are readily obtained with a small bead of borax supported by a loop of platinum wire, are useful blowpipe tests. Borax is also used for soldering metals, for making enamels, for fixing colors on porcelain, and as a flux in various metallurgical processes. The ordinary crystals contain, as above,

$10H_2O$, and belong to the monoclinic system; but the salt can be crystallized with only $5H_2O$ in octahedrons belonging to the isometric system.

301. **Boric Chloride,** BCl_3, can be obtained by passing chlorine gas over an intimate mixture of B_2O_3 and carbon, heated to a red heat in a porcelain retort.

$$B_2O_3 + 3C + 3Cl\text{-}Cl = 3CO + 2BCl_3. \quad [297]$$

It is a very volatile liquid (*Sp. Gr.* 1.35 at 7°), boiling at 17°, and yielding a dense vapor whose Sp. Gr., as found by experiment, is 56.85; chiefly interesting as establishing the quantivalence of boron. It is at once decomposed by water.

$$BCl_3 + 3H_2O = H_3{}^{\equiv}O_3{}^{\equiv}B + 3HCl. \quad [298]$$

302. **Boric Bromide,** BBr_3, prepared like the chloride, is a volatile liquid (*Sp. Gr.* 2.69), boiling at 90°, and giving a vapor whose Sp. Gr. has been found by experiment equal to 126.8. Decomposed by water like the chloride.

303. **Boric Fluoride,** BF_3, is best prepared by intensely heating a mixture of B_2O_3 and fluor-spar.

$$2B_2O_3 + 3CaF_2 = Ca_3{}^{\equiv}O_6{}^{\equiv}B_2 + 2BF_3. \quad [299]$$

A colorless gas, whose Sp. Gr. has been found by experiment equal to 34.2. This gas is eagerly absorbed by water, which dissolves seven hundred times its volume, and forms a corrosive acid liquid called *borofluoric acid*, whose constitution is not well understood. If its composition is that usually assigned to it, its formation will be expressed by the reaction

$$2BF_3 + 3H_2O = B_2O_3 . 6HF. \quad [300]$$

The same compound may be also prepared by dissolving B_2O_3 in $HF + Aq$, and then concentrating the solution.

If borofluoric acid is largely diluted with water, one fourth of the boron separates in the form of boric acid, and there is left in solution what has been called hydrofluoboric acid.

$$(4(B_2O_3 . 6HF) + Aq) \doteq$$
$$2H_3{}^{\equiv}O_3{}^{\equiv}B + (6(HF . BF_3) + 6H_2O + Aq). \quad [301]$$

Hydrofluoboric acid forms salts with basic radicals, and the compound with potassium may be formed by the action of boric acid on a dilute solution of potassic fluoride.

$$(8\,KF + 2\,H_3{=}O_3{=}B + Aq) = 2\,(KF\,.\,BF_3) + (6\,K\text{-}O\text{-}H + Aq). \quad [262]$$

304. **Boron and Hydrogen.** — If magnesium boride, prepared by melting B_2O_3 with twice its weight of magnesium dust, is treated with hydrochloric acid, a gas is evolved which is a mixture of a compound of boron and hydrogen with a large excess of hydrogen gas. This boride of hydrogen resembles in many of its properties the arsenide and antimonide of hydrogen, and its symbol is probably BH_3, but it has not yet been obtained in a pure condition.

305. **Characteristic Reactions.** — The peculiar green color which boric acid imparts to an alcohol or blowpipe flame is the best indication of its presence, and this test is made still more decisive by analyzing the colored light with the spectroscope. The acid, however, must first be set free before the reaction can be obtained. In many of its relations boron resembles carbon.

QUESTIONS AND PROBLEMS.

1. Write the reaction of sulphuric acid on a solution of borax.

2. What test can be applied to determine when an excess of sulphuric acid has been added?

3. Define an ortho acid, regarding orthoboric acid as a type of the class.

4. Make a table showing the relations of the various possible derivatives of boric acid.

5. The empirical symbol of boracite is $Mg_3O_{15}B_8$. What is its rational symbol, and what is its relation to the orthoborates?

6. Boric sulphide, B_2S_3, may be prepared by passing over a mixture of carbon and boric anhydride the vapor of carbonic disulphide, CS_2. The products are $2\,B_2S_3$ and $6\,CO$. Write the reaction.

7. Boric sulphide is readily decomposed by water, giving boric acid and sulphuretted hydrogen. Write the reaction.

8. In reaction [257] what double affinities are called into play?

9. In what respect do you find reaction [262] remarkable?

10. What evidence do you find of the prevailing quantivalence of boron? Are there any facts which would indicate that boron is quinquivalent?

DIVISION XXII.

306. **NITROGEN.** $N = 14$. — Usually trivalent, but also univalent or quinquivalent. Largest constituent of the atmosphere; but to this and the materials of organised beings it is almost exclusively confined. It is the characteristic ingredient of animal tissues, which are composed mainly of the four elements carbon, hydrogen, oxygen, and nitrogen. Vegetable tissues, on the other hand, consist chiefly of only the first three of these elements; but nitrogen is never entirely absent from plants, and is an essential ingredient of many important vegetable products, as, for example, of the albuminoid compounds and of the vegetable alkaloids. Nitrogen is marked by weak affinities, and hence its compounds are usually unstable, as is illustrated by the well-known tendency of animal substance to decay.

307. **Nitrogen Gas**, N_2, constitutes four fifths of the volume of the atmosphere, and can be obtained in a pure condition, — First, by slowly or rapidly burning phosphorus in a confined volume of air. Secondly, by passing air over ignited copper turnings, which combine with the oxygen. Thirdly, by passing chlorine gas through a solution of ammonia: —

$$(8\,H_3N + Aq) + 3\,Cl\text{-}Cl = (6\,H_4NCl + Aq) + N_2. \qquad [261]$$

Fourthly, by heating ammonic nitrite or a mixture of potassic nitrite and ammonic chloride: —

$$(H_4N)\text{-}O\text{-}NO = 2\,H_2O + N_2. \qquad [264]$$

$$K\text{-}O\text{-}NO + (H_4N)Cl = KCl + 2\,H_2O + N_2. \qquad [265]$$

According to Regnault, one litre of nitrogen gas, under standard conditions, weighs 1.256167 grammes. It is remarkable for its inertness, and one of its chief offices in the atmosphere is to moderate the action of its violent associate. The only elementary substances with which it has been observed to combine directly are magnesium, boron, vanadium, and titanium. Nevertheless, nitrogen has a great capacity for combination, and is distinguished by the large number and varied nature of its compounds; but these can only be formed by indirect methods.

Oxides of Nitrogen.*

Nitrogen Monoxide,	N_2O	Hyponitrous Acid,	$H\text{-}O\text{-}\overset{\text{I}}{N}$
Nitrogen Dioxide,	NO		
Nitrogen Trioxide,	N_2O_3	Nitrous Acid,	$H\text{-}O\text{-}\overset{\text{III}}{N}O$
Nitrogen Tetroxide,	NO_2		
Nitrogen Pentoxide,	N_2O_5	Nitric Acid,	$H\text{-}O\text{-}\overset{\text{V}}{N}O_2$

308. **Nitric Acid.** HNO_3. — When electrical discharges are passed through air which is in contact with caustic or carbonated alkalies, or when organic matter decays in the atmosphere under the same conditions,† a partial union of the elements of the atmosphere takes place, and nitrates of potassium, sodium, or calcium are the usual result. From either of these native nitrates, or *nitres*, the acid may be obtained. It is usually prepared by distillation from a mixture of sodic nitrate (§ 148) and sulphuric acid.

$$Na\text{-}O\text{-}NO_2 + H_2\text{=}O_2\text{=}SO_2 = H,Na\text{=}O_2\text{=}SO_2 + H\text{-}O\text{-}NO_2. \quad [266]$$

One molecule of sulphuric acid is adequate to decompose two molecules of nitre; but the temperature required is then much higher, and the nitric acid is in part decomposed. The strongest acid thus prepared is a colorless, fuming liquid, boiling at 86° and freezing at −49°. Its *Sp. Gr.* = 1.552 at 20°. It is unstable, and is partially decomposed when exposed to the light.

$$4\,H\text{-}O\text{-}NO_2 = 2H_2O + 4NO_2 + O\text{=}O. \quad [267]$$

The remaining acid is thus diluted, while the nitric peroxide colors it yellow. A similar decomposition takes place during the distillation of the acid. This decomposition continues until the hydrate $2HNO_3 . 3H_2O$ is formed, which is far more stable, and distils unchanged at 123°. This is the common strong nitric acid of commerce, but it is not a definite compound, the composition varying with the pressure under which the acid distils. A still weaker acid is much used in the arts under the name of aqua-fortis. The strength of the acid may be determined from its specific gravity, by means of tables prepared for the purpose.

* In the absence of any definite knowledge in regard to the molecular structure of the oxides of nitrogen, we cannot use more significant names.

† It has been rendered probable by recent investigation that nitrification is a variety of fermentation, connected with the life of certain lower organisms in the soil.

Sp. Gr.	Per Cent HNO_3	Sp. Gr.	Per Cent HNO_3	Sp. Gr.	Per Cent HNO_3
1.500	92.36	1.395	64.17	1.228	36.25
1.470	82.71	1.343	51.50	1.165	26.95
1.435	73.10	1.299	45.62	1.105	17.62

Nitric acid is one of the most corrosive agents known. With a very few exceptions, it oxidizes all the elementary substances, converting them into oxides, acids, or nitrates, as the case may be. In these reactions, as a general rule, nitric oxide is evolved; but the products vary to a certain extent with the conditions of the experiments, and examples will be found under the different elements, and also in [110, 271, 279, and 287], illustrating the different phases which the reaction may assume. Nitric acid corrodes all organic tissues, oxidizing them, and forming various products, among which the most common are water, carbonic dioxide, and oxalic acid. When more dilute, it stains the skin, wool, silk, and other albuminoid bodies a bright yellow color. Very strong nitric acid, when mixed with strong sulphuric acid, acts on some organic compounds in a very remarkable way. It removes one or more atoms of hydrogen, and substitutes an equal number of atoms of the radical NO_2 in their place.

$$\underset{\text{Benzol.}}{C_6H_6} + H\text{-}O\text{-}NO_2 = \underset{\text{Nitrobenzol.}}{C_6H_5(NO_2)} + H_2O. \qquad [268]$$

With the various bases it forms a large class of important salts. When the radical is univalent, these salts have the general symbol $\overset{\text{I}}{R}\text{-}O\text{-}NO_2$. When the radical is bivalent, the general formula becomes $\overset{\text{II}}{R}\text{-}O_2\text{-}(NO_2)_2$, or $\overset{\text{II}}{R}\text{-}O_2\text{-}N_2O_4$. Salts of these types are, in the ordinary use of the term, the normal, or ortho nitrates; but, theoretically, nitrogen is capable of fixing five univalent radicals, and hence some chemists regard the assumed compound $H_6^{\text{I}}O_3^{\text{II}}N$ as orthonitric acid, and salts of that type as orthonitrates. By eliminating from this ortho-acid first one and then two molecules of water, we obtain the following anhydrides, the last of which is the ordinary acid:—

Orthonitric Acid,	$H_6^{\text{I}}O_3^{\text{II}}N$,	or	$H\text{-}O\text{-}NO_2 . 2H_2O$
Metanitric "	$H_3^{\text{I}}O_3^{\text{II}}NO$,	or	$H\text{-}O\text{-}NO_2 . H_2O$
Dimetanitric "	$H\text{-}O\text{-}NO_2$		

Salts are known whose symbols may be written on all these types, but they may also be written on the ordinary type as well. Thus,

$H_2Bi^{\equiv}O_3^{\equiv}N$ or $Bi^{=}O_3^{=}NO_2.H_2$

Dihydro-bismuthic Orthonitrate. Basic bismuthic Nitrate.

$Mg_3^{\equiv}O_6^{\equiv}(NO)_2$ or $(Mg\text{-}O\text{-}Mg\text{-}O\text{-}Mg)^{=}O_2^{=}(NO_2)_2$

Magnesic Metanitrate. Trimagnesic Nitrate.

Such distinctions are of no practical importance, but they are of value in pointing out the many-sided relations of our subject. Under no condition does potassic hydrate form more than one salt with nitric acid, and the important theoretical bearing of this fact is evident.

309. **Nitrogen Pentoxide,** N_2O_5, the anhydride of nitric acid, may be obtained by passing dry chlorine gas over dried argentic nitrate heated to 95°.

$$4\,AgNO_3 + 2\,Cl\text{-}Cl = 4\,AgCl + 2\,N_2O_5 + O\text{=}O. \qquad [269]$$

It is a white solid, crystallizing in prisms of the fourth system, melting at 29°.5, and boiling at 45°. Very unstable, undergoing spontaneous decomposition in a sealed glass tube. By the action of water it forms nitric acid.

$$N_2O_5 + H_2O = 2\,HNO_3. \qquad [270]$$

310. **Nitrous Acid,** $H\text{-}O\text{-}NO$, is not known in the pure state, and the aqueous solution rapidly undergoes decomposition when diluted or warmed. The salts of this acid, however, the *nitrites*, are, on the contrary, very stable bodies. They may be formed by the action of the acid upon hydrates or oxides, but more readily by the reduction of the nitrates. Thus potassic nitrite is prepared by fusing nitre with metallic lead or copper. Nitrites are found dissolved in natural waters, and ammonic nitrite exists at times in minute quantities in the atmosphere. Argentic nitrite is difficultly soluble in cold water, and is precipitated when argentic nitrate is added to a solution of an alkaline nitrite, if not too dilute. This reaction, and the evolution of red fumes when treated with dilute acids, readily distinguish the nitrites from the nitrates. Compare also § 312.

311. **Nitrogen Trioxide,** N_2O_3, is the anhydride of nitrous acid. Best prepared by the action of dilute nitric acid (*Sp. Gr.* 1.25) on starch. Is also formed in the following reactions:—

$$As_2O_3 + 2\,HNO_3 = As_2O_5 + N_2O_3 + H_2O. \qquad [271]$$

$$2\,Ag\text{-}Ag + 6\,HNO_3 = 4\,AgNO_3 + N_2O_3 + 3\,H_2O. \qquad [272]$$

$$4\,\mathbb{N}\mathbb{O} + \mathbb{O}\text{-}\mathbb{O} = 2\,N_2O_3. \qquad [273]$$

In each case brownish red fumes are formed, which, at a low temperature, become condensed into a very volatile blue liquid, boiling at about 0°. With a small quantity of water it yields nitrous acid, *H-O-NO*, but a large quantity at once decomposes it.

$$3\,N_2O_3 + H_2O = 4\,NO + 2\,HNO_3. \qquad [274]$$

If the red vapor is passed into a solution of potassic hydrate, we obtain potassic nitrite, and in a similar way other nitrites may be made.

$$(2\,KOH + Aq) + N_2O_3 = (2\,K\text{-}O\text{-}NO + H_2O + Aq). \qquad [275]$$

According to the theory of the last section, ordinary nitrous acid is the first anhydride of an assumed acid, $H_3{}^{\equiv}O_3{}^{\equiv}N$. This would be called orthonitrous acid, and the ordinary acid would then be metanitrous acid. The compound $Pb_3{}^{\equiv}O_6{}^{\equiv}N_2$, according to this view, is plumbic orthonitrite, but it may be also regarded as a triplumbic nitrite of the ordinary type $(Pb\text{-}O\text{-}Pb\text{-}O\text{-}Pb)^{=}O_2{}^{=}(NO)_2$.

312. **Hyponitrous Acid**, *H-O-N*, has not been isolated, but the potassium salt is formed by the action of sodium amalgam on a solution of potassium nitrite.

$$K\text{-}O\text{-}NO + H_2 = K\text{-}O\text{-}N + H_2O. \qquad [276]$$

On neutralizing with acetic acid the solution, — rendered alkaline by the *Na-O-H* formed at the same time, — and then adding argentic nitrate, a yellow and almost insoluble precipitate is obtained, which is *Ag-O-N*.

313. **Nitrogen Monoxide**, N_2O. — This compound, commonly called nitrous oxide, is best prepared by gently heating ammonic nitrate in a glass flask or retort.

$$NH_4\text{-}O\text{-}NO_2 = 2\,H_2O + N_2O. \qquad [277]$$

It may also be obtained by exposing nitrogen dioxide gas to the action of moistened iron filings, which absorb one half of the oxygen.

$$4\,NO - O^{=}O = 2\,N_2O. \qquad [278]$$

It is also evolved when zinc dissolves in dilute nitric acid, or, more surely, when a mixture of equal parts of nitric and sulphuric acids, diluted with eight or ten parts of water, is used for dissolving the

$$4\,Zn + (10\,HNO_3 + Aq) = (4\,Zn(NO_3)_2 + 5\,H_2O + Aq) + N_2O. \quad [279]$$

Nitrogen monoxide is a colorless gas (Sp. Gr. 22), which, by pressure and cold, may be condensed to a colorless liquid, boiling at —88° and freezing by its own evaporation at about —101°. It is less stable than nitric oxide. It is decomposed by heat, and all combustibles burn in it with nearly the same readiness and brilliancy as in pure oxygen gas. When pure, it can be inhaled without danger, and is much used as an anæsthetic agent. With some patients it produces at first a transient intoxication, attended at times with uncontrollable laughter. Hence the popular name of laughing-gas. It manifests no tendency to unite with more oxygen. It is soluble in water to a limited extent, and to a much greater degree in alcohol. At 0° one volume of water dissolves 1.3 volumes, and one volume of alcohol 4.18 volumes, of this gas.

314. **Nitrogen Dioxide,** *NO*, commonly called *Nitric Oxide*, is best prepared by the action of dilute nitric acid (*Sp. Gr.* about 1.2) on copper turnings.

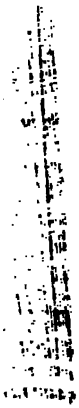
$$3\,Cu + (8\,HNO_3 + Aq) = (3\,Cu(NO_3)_2 + 4\,H_2O + Aq) + 2\,NO. \quad [280]$$

The reaction appears to consist, first, in a metathesis of the metal with the hydrogen of the acid; and, secondly, in the reduction of a further portion of the acid by the hydrogen thus liberated. In order to obtain a pure product it is important that the acid should be in excess. Nitrogen dioxide may also be obtained perfectly pure by heating together a mixture of ferrous chloride, nitre, and hydrochloric acid.

$$(6\,FeCl_2 + 2\,KNO_3 + 8\,HCl + Aq) = (3\,[Fe_2]Cl_6 + 2\,KCl + 4\,H_2O) + 2\,NO. \quad [281]$$

A mixture of ferrous sulphate, nitre, and dilute sulphuric acid (*Sp. Gr.* 1.18) may also be used.

Nitric oxide is a colorless permanent gas (Sp. Gr. = 15), but slightly soluble in water (one volume of water dissolves one twentieth of a volume of *NO*). It extinguishes a burning candle, but both phosphorus and charcoal, if burning vigorously, continue to burn, and with great intensity, when plunged into the gas. It is the most stable of the oxides of nitrogen, and is not decomposed by a red heat. It is



in other reactions of nitric acid on the metals, the main
re or less mixed with other oxides of nitrogen.

chlorides of Nitrogen. — If in reaction [242] no gold or
present to unite with the chlorine evolved by the aqua-
ement combines with the nitric oxide set free at the same
sides chlorine gas we obtain, as products of the reaction,
which we may call nitrous oxychloride or nitrosyl chlo-
).

$$+ 3\,HCl + Aq) = (2\,H_2O + Aq) + NOCl + Cl\text{-}Cl. \quad [288]$$

products of this reaction are cooled by a freezing mixture,
colored liquid is obtained, boiling at −7°, which appears to
re of free chlorine and nitrosyl chloride in varying propor-
if the same products are passed into strong sulphuric acid,
yl chloride is absorbed while the chlorine escapes. There is
ed $H,NO\text{-}SO_4$, and, if this nitrosyl sulphate is heated with
re $NOCl$ is evolved. Nitrosyl chloride can also be obtained
direct union of nitric oxide and chlorine. It is an orange-
as, which readily liquefies when cooled by a freezing mixture.
id has a deep orange color and boils at −8°. There is also a
bromide.

xyl Chloride, NO_2Cl, is obtained by acting on phosphoric oxy-
ride with plumbic nitrate, —

$$3\,Pb(NO_3)_2 + 2\,POCl_3 = Pb_3(PO_4)_2 + 6\,NO_2Cl. \quad [289]$$

compound is a heavy yellow liquid, which boils at 5°, and is
mposed by water into nitric and hydrochloric acids.

17. **Compounds with Hydrogen. — Ammonia Gas.** NH_3. —
rogen and hydrogen gases will not directly combine; but through
ious indirect methods, not well understood, this union is constantly
ing place in nature, and ammonia gas is the chief product. This
, or some one of its numerous compounds, is constantly formed
henever an organic substance decays or is charred, as in the process
dry distillation. It is also formed in many chemical reactions when
trogen and hydrogen atoms are brought together at the moment of
emical change. Thus, when a mixture of nitric oxide and hydrogen
as is passed over heated platinum sponge, we have the reaction

$$2\,NO + 5\,H\text{-}H = H_2O + 2\,NH_3. \quad [290]$$

So also when nitric acid is added in very small quantities at a time to a mixture of zinc and dilute hydrochloric acid, from which hydrogen gas is being slowly evolved, we have the reaction

$$HNO_3 + 4\,H\text{-}H = NH_3 + 3\,H_2O. \qquad [291]$$

But the ammonia thus produced unites at once with the hydrochloric acid present to form ammonic chloride, and in a similar way ammonium salts are frequently formed to a limited extent when zinc and similar metals are dissolved in nitric acid. Practically, we always prepare ammonia gas from the commercial ammonic chloride by the reaction

$$2\,NH_4Cl + Ca{=}O_2{=}H_2 = CaCl_2 + 2\,H_2O + 2\,NH_3. \qquad [292]$$

It is a colorless gas, so light (**Sp. Gr.** 0.591) that it can be collected in an inverted bottle by displacement. By pressure and cold it may be readily condensed to a liquid, which boils at −38°.5 and freezes at −75°. The evaporation of the liquefied gas is attended with great reduction of temperature, and this principle is applied in the apparatus of Carré to the artificial production of cold. Ammonia has a familiar pungent odor, and is useful in medicine as an irritant, but when pure it is wholly irrespirable. It is incombustible in air, but burns in an atmosphere of oxygen, yielding aqueous vapor and nitrogen gas.

The composition of ammonia gas may be thus ascertained. First, by passing a series of electrical discharges through a confined volume of the gas in a eudiometer, the volume doubles.

$$2\,NH_3 = N{\equiv}N + 3\,H\text{-}H. \qquad [293]$$

If next we add to this product one half of its volume of oxygen gas, then explode the mixture, and subsequently remove with pyrogallic acid the residual oxygen, we shall find that the volume of nitrogen gas remaining in the tube is exactly one half of the volume of the ammonia gas with which we started. Secondly, if we shake up in a eudiometer tube a measured volume of chlorine gas with a weak solution of aqua ammonia, taking care after the reaction is finished to expel by heat all the nitrogen from the liquid, it will be found that the volume of chlorine has been replaced by one third of its volume of nitrogen gas.

With colored test-paper, ammonia gas, even when dry, gives a strong

action, and it directly combines with several of the acid These unimportant compounds, however, must not be d with the important class of ammonium salts. In part pond to the amides mentioned below, but the constitution is not well understood. The last are frequently called am- and of these sulphuric ammonide, $(NH_2)_2 . SO_2$, will serve ample. Ammonia gas forms also equally anomalous com- with many anhydrous metallic salts. Thus, argentic and lorides absorb large volumes of ammonia gas, forming what be molecular compounds, $AgCl . 2\,H_3N$ and $CaCl_2 . 8\,H_3N$, the ammonia seems to play somewhat the same part as water llization in ordinary salts. But by far the most important f ammonia is its power of combining directly with water and e acids, as such, to form the large class of ammonium salts. ing these compounds, however, nitrogen changes its quanti- , and it will therefore be convenient to class them under a t head. When ammonia gas comes in contact with the fumes olatile acid, the formation of the ammonium salt gives rise to white smoke, which is one of the most characteristic tests for bstance.

8. **Amines, or Compound Ammonias.** — Ammonia gas is the of a large class of compounds, most of them volatile, in all of h nitrogen is trivalent. These compounds may be regarded as ed from one or more molecules of ammonia, by replacing the rogen atoms either wholly or in part with various positive radicals. rding as they are fashioned after the type of one, two, three, or molecules of ammonia, they are called monamines, diamines, etc., they are distinguished as primary, secondary, or tertiary, accord- as one, two, or three hydrogen atoms in the monamines, or the responding groups of atoms in the polyamines, have been replaced. may represent the type of ammonia as in the table below, which tains the symbols of a few of the compound ammonias.

Monamines.

	Primary.		*Secondary.*		*Tertiary.*
$\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N$	$\left.\begin{matrix} CH_3 \\ H \\ H \end{matrix}\right\} N$	$\left.\begin{matrix} C_6H_5 \\ H \\ H \end{matrix}\right\} N$	$\left.\begin{matrix} C_2H_5 \\ C_2H_5 \\ H \end{matrix}\right\} N$	$\left.\begin{matrix} C_6H_5 \\ C_2H_5 \\ H \end{matrix}\right\} N$	$\left.\begin{matrix} CH_3 \\ C_2H_5 \\ C_6H_5 \end{matrix}\right\} N$
mmonia.	Methylamine.	Phenylamine. (Aniline.)	Diethylamine.	Phenyl-ethyl-amine.	Methyl-ethyl-phenyl-amine.

Diamines.

Primary.

$\left.\begin{matrix} H_2 \\ H_2 \\ H_2 \end{matrix}\right\} N_2$

Ammonia doubly condensed.

$\left.\begin{matrix} C_2H_4 \\ H_2 \\ H_2 \end{matrix}\right\} N_2$

Ethylene diamine.

Tertiary.

$\left.\begin{matrix} C_2H_4 \\ C_2H_4 \\ (C_2H_5)_2 \end{matrix}\right\} N_2$

Diethylene-diethyl-diamin.

Many of the ammoniated compounds of the metals may be arranged under this same type. Thus, when potassium is heated in dry ammonia gas, an olive-green compound is formed, which has the composition K_2H_2N;* and other examples will be given hereafter.

The amines are all basic, and, like ammonia gas, combine directly with acids to form salts; but this character is the less strongly marked in proportion as the hydrogen atoms have been replaced. The volatile organic bases belong to the same class of compounds.

319. **Amides.** — The atoms of hydrogen in ammonia gas may be replaced by negative as well as by positive radicals; but then the product, instead of being basic, is either neutral or acid. These compounds are classified and named like the amines, but with few exceptions only one, or one set, of the hydrogen atoms can be thus replaced. The following are a few examples: —

Monamides.

$\left.\begin{matrix} C_2H_3O \\ H \\ H \end{matrix}\right\} N$

Acetamide.

$\left.\begin{matrix} C_7H_5O \\ H \\ H \end{matrix}\right\} N$

Benzamide.

Diamides.

$\left.\begin{matrix} C_2O_2 \\ H_2 \\ H_2 \end{matrix}\right\} N_2$

Oxamide.

$\left.\begin{matrix} C_4H_4O_2 \\ H_2 \\ H_2 \end{matrix}\right\} N_2$

Succinamide.

These compounds may also be regarded as formed by the union of the compound radical amidogen (H_2N) with the acid radical, and hence the name *amides*. They differ, then, from the corresponding acids only in containing amidogen in place of hydroxyl. Thus,

$Ho\text{-}C_2H_3O$	$Ho_2\text{-}CO$	$Ho_2\text{-}C_2O_2$	$Ho_2\text{-}C_4H_4O_2$
Acetic Acid.	Carbonic Acid.	Oxalic Acid.	Succinic Acid.
$H_2N\text{-}C_2H_3O$	$(H_2N)_2\text{-}CO$	$(H_2N)_2\text{-}C_2O_2$	$(H_2N)_2\text{-}C_4H_4O_2$
Acetamide.	Carbamide (Urea).	Oxamide.	Succinamide.

These amides are all neutral; but if in the dibasic acids we replace only one of the atoms of hydroxyl, it is evident that we shall obtain a

* This compound, although an amine as here classified, has always been called Potassamide.

class of amides still containing an atom of basic hydrogen, and which are therefore acids. Thus are formed

$HO,H_2N{=}CO$ — Carbamic Acid.* $HO,H_2N{=}C_2O_2$ — Oxamic Acid. $HO,H_2N{=}C_4H_4O_2$ — Succinamic Acid.

Lastly, if we take an acid like lactic acid, $\overset{+}{H}O,\overline{H}O{=}C_3H_4O$, or glycolic acid, $\overset{+}{H}O,\overline{H}O{=}C_2H_2O$, which, although diatomic, is only monobasic (§ 44), we can obtain from each acid, at least theoretically, two distinct amides, according as we replace the basic hydrogen ($\overset{+}{H}$) or the alcoholic hydrogen ($\overline{H}$). See § 44. The first will be neutral, the second acid; but although several of the acid amides are known, the only neutral amide of this class which has been investigated is that derived from lactic acid.

$NH_2,\overline{H}O{=}C_3H_4O$ — Lactamide (Neutral). $\overset{+}{H}O,NH_2{=}C_3H_4O$ — Lactamide (Acid). $\overset{+}{H}O,NH_2{=}C_2H_2O$ — Glycolamide (Acid) or Glycocol.

From these various amides a large number of compounds may be derived by replacing the hydrogen atoms either of the amidogen or of the acid with different compound radicals. The following are a few examples: —

$\left.\begin{matrix}C_7H_5O\\C_6H_5\\H\end{matrix}\right\}N$ — Phenyl-benzamide. $\left.\begin{matrix}C_2O_2\\(C_2H_5)_2\\H_2\end{matrix}\right\}N_2$ — Diethyl-oxamide. $\left.\begin{matrix}((C_2H_5)O{-}C_2O_2)\\H\\H\end{matrix}\right\}N$ — Oxamethane.

$\left.\begin{matrix}HO{-}C_2H_2O\\C_7H_5O\\H\end{matrix}\right\}N$ — Hippuric Acid. $\left.\begin{matrix}HO{-}C_3H_4O\\C_2H_5\\H\end{matrix}\right\}N$ — Lactethylamide. $\left.\begin{matrix}(C_2H_5)O{-}C_3H_4O\\H\\H\end{matrix}\right\}N$ — Lactmethane.

The last two compounds are isomeric, the only difference being that in the first the radical ethyl replaces an atom of hydrogen of the amidogen, while in the second it replaces the alcoholic hydrogen of the lactic acid. That there is a real difference between the two is proved by the following reactions: —

$$\left.\begin{matrix}(C_2H_5)O{-}C_3H_4O\\H\\H\end{matrix}\right\}N+K{-}O{-}H=K,\underset{\text{Potassic Ethyl-lactate.}}{(C_2H_5){-}O_2{-}C_3H_4O}+\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \quad [294]$$

$$\left.\begin{matrix}HO{-}C_3H_4O\\C_2H_5\\H\end{matrix}\right\}N+K{-}O{-}H=K,\underset{\text{Potassic Lactate.}}{H{-}O_2{-}C_3H_4O}+\underset{\text{Ethylamine.}}{\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N} \quad [295]$$

* The acid has not been isolated, but the ammonic salt is well known.

[illegible]—When an acid monamide we eliminate a molecule of water, as if from a normal. Similarly we eliminate a molecule of an amide gas we obtain as the product a compound which may be regarded as formed by the union of the acid radical with the imidogen radical [illegible]. Thus,

[illegible] [29]

[illegible] [30]

Such compounds are called [illegible], and they always act as monobasic acids.

[illegible]—If from a normal monamide we eliminate a molecule of water, the residue, which may be regarded as a compound of nitrogen with a monobasic radical, has been called a Nitrile. Thus,

[illegible] [31]

[illegible] [32]

These compounds are weak bases, like ammonia, combining directly with acids to form salts, and from one point of view they may be regarded as formed from another as ammonia.

[illegible] **Ammonium Compounds.**—In all the above compounds [illegible] one or more of the hydrogen atoms of the ammonia molecule [illegible] and neither more than three atoms of hydrogen [illegible] monamine radicals. But when the latter ammonias are brought in contact with acids, the nitrogen atom [illegible] manifest two additional affinities, and a most important class of compounds is formed in which nitrogen is pentequivalent. The cause of this evident accession of power is not well understood, but it is [illegible] to the united influence which the negative atoms or radicals of the acids exert. In all these cases the ammonias combine with the acids as a whole, and the reaction is an example of synthesis and not of metathesis. The following are a few examples:—

$N H_3 + H Cl = N H_4 . Cl = N H_4 Cl$ (Ammonic Chloride.) like $K Cl$. [33]

$N H_3 + H_2 O = N H_4 . H O = N H_4 \text{-} O \text{-} H$ (Ammonic Hydrate.) like $K \text{-} O \text{-} H$. [34]

$N H_3 + H N O_3 = N H_4 . (N O_3) = N H_4 \text{-} O \text{-} N O_2$ (Ammonic Nitrate.) like $K \text{-} O \text{-} N O_2$. [35]

$$(N{\equiv}H_3)_2 + H_2{=}SO_4 = N_2{\cdot}H_8{,}(SO_4) = (NH_4)_2{=}O_2{=}SO_2 \text{ like } K_2{=}O_2{=}SO_2. \quad [303]$$

Ammonic Sulphate.

The products thus obtained resemble very closely the salts of the alkaline metals. With certain limitations they are susceptible of the same reactions, and in these reactions the atomic group NH_4 plays the same part as the metallic atoms in the other salts. Thus we have

$$(Ag{-}NO_3 + NH_4{-}Cl + Aq) = AgCl + (NH_4{-}NO_3 + Aq). \quad [304]$$

$$(CaCl_2 + (NH_4)_2{=}O_2{=}CO + Aq) = Ca{=}O_2{=}CO + (2NH_4Cl + Aq). \quad [305]$$

Hence we conclude that the ammonium salts are compounds of this univalent radical which we call ammonium, and therefore we write their symbols as above. But although many attempts have been made to obtain the radical substance corresponding to NH_4, these attempts have been hitherto unsuccessful. It is true that when we electrolyze a solution of ammonic chloride, using as the negative pole of the battery a quantity of mercury, we obtain a material resembling a metallic amalgam, which, when kept, slowly changes back to metallic mercury, evolving a mixture of hydrogen and ammonia gases; but it would now appear that in this pasty mass the gases are merely mixed, and not chemically combined, and, moreover, the total amount of material which the mercury thus singularly encloses is exceedingly small.

323. **Ammonic Chloride (Sal Ammoniac)**, NH_4Cl, is the most important of the ammonium salts, and the material from which the other ammonium compounds are prepared. It is manufactured in large quantities from the ammoniacal liquid of the gas works, one of the products of the dry distillation of coal. It is a white crystalline salt, very soluble in water, but only slightly soluble in alcohol. It sublimes below redness without first melting. It is isomorphous with sodic and potassic chloride, and resembles these salts, especially the last, very closely. Like potassic chloride, it is precipitated from aqueous solutions by platinic chloride, with which it forms a double salt difficultly soluble in water and still less soluble in alcohol.

$$(2\,NH_4Cl + PtCl_4 + Aq) = (NH_4Cl)_2\,.\,PtCl_4 + (Aq). \quad [306]$$

324. **Ammonic Hydrate (Aqua Ammonia).** $(NH_4{-}O{-}H + Aq.)$ — At 0° water absorbs 1,050 times its own volume of ammonia gas; but the quantity absorbed rapidly diminishes as the temperature rises, so that at 15° it can only hold 727 times its volume, and at 24°, 600

times its volume. Water saturated at 15° contains about one third of its weight of ammonia, but, in consequence of the great expansion which attends the absorption, the solution is lighter than water. This solution has the pungent odor of ammonia, because the gas slowly escapes even at the ordinary temperature of the air, and by prolonged boiling the whole may be driven off. In this and in other physical relations the compound of ammonia with water acts like the solution of a gas, but in all its chemical relations it behaves like an alkaline hydrate. It is strongly caustic; it precipitates metallic hydrates from solutions of their salts; it saponifies fats; and it is very much used in the laboratory as an alkaline reagent. It has been called the *volatile alkali*. It differs, however, from *the fixed alkalies, soda and potash*, in two important particulars. First, it is decomposed by heat into ammonia gas and water, and is not, therefore, properly speaking, volatile. Secondly, it forms with many metallic radicals soluble double salts, and other compounds of peculiar constitution, which can have no counterparts among the compounds of the alkaline metals. Hence it is that in many important particulars the reactions of the ammonium salts are wholly different from those of the corresponding salts of sodium and potassium. They either do not give precipitates under the same conditions, or the precipitates obtained have a wholly different character. Compare [304], [305], with §§ 249, 259, and 225.

325. **Ammonic Carbonate.** — The commercial salt is a *translucent* white solid, obtained by subliming a mixture of sal ammoniac with chalk. It is very soluble in water, has the odor of ammonia, and a strong alkaline reaction. Its composition is not unvarying, but the usual product appears to be a mixture of hydro-ammonic carbonate and ammonic carbamate (§ 319) in equivalent proportions. Exposed to the air it loses about 44 per cent of its weight, owing to the dissipation of the ammonic carbamate, which is resolved into CO_2 and NH_3, and the *opaque spongy* residue consists of hydro-ammonic carbonate. From the commercial salt there may be prepared well-defined crystals of the three following compounds: —

Acid or Hydro-ammonic Carbonate, $H,NH_4{=}O_2{=}CO$
Neutral or Diammonic Carbonate, $(NH_4)_2{=}O_2{=}CO\,.\,H_2O$
Dihydro-tetra-ammonic Tricarbonate, $H_2(NH_4)_4{}^{VI}O_6{}^{VI}(CO)_3\,.\,H_2O$

A solution of the neutral salt prepared by mixing a solution of the commercial substance with the requisite amount of aqua ammonia is very much used in the laboratory as a reagent.

326. **Characteristic Reactions of the Ammonium Salts.** — These compounds, when heated with caustic alkalies or alkaline earths, give off ammonia gas, which may be recognized by its odor, or by the cloud it forms with *HCl*. The ammonium salts are all volatile — with or without decomposition — at a moderate temperature (except in the few cases in which the acid is fixed), and are thus readily distinguished from those of the non-volatile bases. This quality is of great importance in chemical analysis, and leads us to select the ammonium salts, whenever it is possible, as reagents, because the excess of the reagent and all the ammoniacal products can so readily be eliminated by heat.

327. **Ammonium Bases.** — The salts formed by the union of the compound ammonias, or amines, with acids, closely resemble those formed from ammonia, and may be regarded as consisting of radicals derived from ammonium by replacing one or more of its hydrogen atoms with other positive radicals. Of these compounds the most interesting are those corresponding to ammonic hydrates, but in which all four of the hydrogen atoms have been thus replaced. They may be prepared from the tertiary amines in a manner which is illustrated by the following reactions: —

$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\} N + (C_2H_5)I = \left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\} N\text{-}I \qquad [307]$$

Triethylamine. Tetrethyl-ammonic Iodide.

$$Ag_2O + 2\,[(C_2H_5)_4N\text{-}I] + H_2O = 2\,AgI + 2\,([(C_2H_5)_4N]\text{-}O\text{-}H). \qquad [308]$$

The solutions of the amines in water, although, like aqua ammonia, they may be regarded as compounds of an ammonium radical, are decomposed when evaporated into the volatile amine and water, and it might have been anticipated that the tetra-ethyl-ammonic hydrate would break up in a similar way, but such is not the case. This compound is stable, and on evaporating the solution resulting from the last reaction the hydrate is obtained as a white solid resembling caustic potash. It absorbs water and carbonic dioxide from the air; it precipitates the metallic oxides or hydrates from their salts; it saponifies fats; and it neutralizes the strongest acids, just as potassic hydrate does. Several similar compounds have been prepared; and since it appears that the four hydrogen atoms of ammonium may be replaced by the same or by different atoms at will, it is evident that an infinite number of such compounds are, theoretically at least, possible. These hydrates have a bitter taste,

and cannot be volatilized without decomposition. In both of these particulars they very closely resemble the non-volatile organic alkaloids, which are evidently formed after the same type. There are, therefore, two classes of bases derived from ammonia; the one volatile, after the type of H_3N; the other non-volatile, after the type of $NH_4{\cdot}O{\cdot}H$; and corresponding to these there are two classes of organic alkaloids, the first volatile, like nicotine and conine, the second non-volatile, like quinine and morphine. In all these bases the parts are grouped around one or more atoms of nitrogen, and the difference between the two classes of compounds depends primarily on the fact that these atoms are trivalent in the first class and quinquivalent in the second. The two classes of compounds are, however, intimately related, and may be regarded from different points of view. Thus the amides, imides, and nitriles, which we have considered as formed after the type of ammonia gas, may also be regarded as anhydrides of the salts of the ammonium radicals, and in many cases may be prepared from these salts by a simple process of dehydration. Moreover, careful study will open up many other relations of these bodies, all of which must be considered before we can command a comprehensive view of the subject.

328. **Chloride of Nitrogen,** NCl_3, is a very volatile yellow, oily liquid, obtained by the action of chlorine gas on a strong solution of sal ammoniac.

329. **Bromide of Nitrogen,** NBr_3, is obtained by digesting bromide of potassium with chloride of nitrogen, and is similar to the last in appearance, but has a much darker color.

330. **Iodide of Nitrogen,** NI_3, is a black powder, formed when aqua ammonia is added in large excess to an alcoholic solution of iodine. The chloride, bromide, and iodide of nitrogen are all highly explosive, and illustrate in a most marked manner the instability of endothermous compounds (§ 74).

331. **PHOSPHORUS.** $P = 31$. — Found in nature, chiefly in combination with calcium, in calcic phosphate, a mineral substance very widely but sparingly disseminated, and an essential but subordinate constituent of many plants, and of all the higher animal structures. In order to obtain the elementary substance, the calcic phosphate (generally bone ashes) is first partially decomposed with sulphuric acid. The *soluble* acid calcic phosphate thus obtained is easily separated from the nearly *insoluble* calcic sulphate, by filtration. The solution is then evaporated, the acid phosphate mixed with pulverized charcoal, and the

thoroughly dried mass distilled in earthen retorts. The distillation proceeds slowly, and requires a very high temperature.

$$Ca_3^{III}O_6^{III}(PO)_2 + 2\,H_2^{-}O_2^{-}SO_2 = 2\,Ca^{=}O_2^{-}SO_2 + H_4Ca^{III}O_6^{III}(PO)_2.$$

When dried, $$H_4Ca^{III}O_6^{III}(PO)_2 = Ca^{=}O_2^{-}(PO_2)_2 + 2\,H_2O, \qquad [309]$$

$$3\,Ca^{=}O_2^{-}(PO_2)_2 + C_{10} = Ca_3^{III}O_6^{III}(PO)_2 + 10\,CO + P_4.$$

332. **Common Phosphorus,** P_4, when perfectly pure, is a colorless, transparent solid; but ordinarily it has a yellowish tint, and is only translucent. At low temperatures it is brittle, but at 20° it is soft, like wax. It melts at 45°, and boils at 290°. *Sp. Gr.* of solid, 1.83. Insoluble in water, slightly soluble in alcohol and ether, still more soluble in both the fixed and volatile oils, and very soluble in carbonic disulphide or sulphurous chloride. Phosphorus is by far the most combustible of the chemical elements. It takes fire below the boiling point of water, and slowly combines with the oxygen of the air at the ordinary temperature. If in not too small quantity, the heat evolved by its slow combustion soon raises the temperature to the point of ignition, and it is therefore always preserved under water or alcohol. The product of the rapid combustion is phosphoric pentoxide; that of the slow combustion in moist air, chiefly phosphorous acid. Exposed to the air in the dark, phosphorus emits a greenish light, and hence its name, from φῶς φορός; but this phosphorescence, though always accompanying the slow combustion, does not appear to be necessarily connected with it. Sticks of phosphorus, when kept under water, become covered after some time with a white crust, which consists of a mass of microscopic crystals; and in the course of many years these crystals may acquire considerable size. The form of the crystals is the regular dodecahedron of the first system (Fig. 26), and crystals of the same form are obtained by slowly evaporating the solution of phosphorus in carbonic disulphide.

333. **Red Phosphorus.** — Exposed to the direct sunlight under water, phosphorus becomes covered with a red coating, and the same red modification is formed in great abundance when ordinary phosphorus is heated for several hours to a temperature between 235° and 250° in an atmosphere of carbonic dioxide, or some other inert gas. Red phosphorus is insoluble in carbonic disulphide, and is thus easily separated from the portion which has not been changed. Iodine facilitates the conversion, and if a solution of phosphorus in carbonic disulphide

containing a little iodine is sealed up in a glass flask and heated for some time to only 100°, red phosphorus is slowly precipitated. As usually obtained, red phosphorus is an amorphous powder; but it has been crystallized, and it appears that the crystals are rhombohedrons belonging to the third system. Hence phosphorus is dimorphous, and in this respect resembles arsenic and antimony. The *Sp. Gr.* of red phosphorus is about 2.1. It undergoes no change in dry air, and may even be heated to 250° without taking fire; but at a slightly higher temperature it changes back to common phosphorus and inflames. The specific heat of red phosphorus is 0.1700, while that of the ordinary variety is 0.1387; and hence, as we should anticipate, this reverse change is attended with the evolution of heat. Moreover, the calorific power of common phosphorus is to that of red phosphorus in the proportion of 1.15 to 1. In general, red phosphorus is less active, chemically, than common phosphorus, and is not, like the latter, poisonous. Both varieties are largely used in the manufacture of friction matches. The red variety is not used in making the match itself, but only in the preparation of the surface on which it is rubbed.

334. **Phosphorus and Oxygen.** — The following compounds of phosphorus with oxygen, or with both oxygen and hydrogen, have been observed. We give the usual names, but the student is now in position to devise a more philosophical nomenclature.

Phosphorous Trioxide,	P_2O_3
Phosphorous Pentoxide,	P_2O_5
Hypophosphorous Acid,	$H\text{-}O\text{-}(P{=}O,H_2)$
Phosphorous Acid,	$H_2{=}O_2{=}(P{=}O,H)$
Common Phosphoric Acid,	$H_3{=}O_3{=}(P{-}O)$
Metaphosphoric Acid,	$H\text{-}O\text{-}(P{=}O_2)$
Pyrophosphoric Acid,	$H_4{=}O_4{=}(P{-}O_2{=}P)$
Sodium Salt of Hexabasic Acid,	$Na_6{}^{\text{vi}}O_6{}^{\text{vi}}(P{-}O_2{-}P{-}O_2{-}P{-}O_2{-}P)$
Sodium Salt of Dodecabasic Acid,	$Na_{12}{}^{\text{xii}}O_{12}{}^{\text{xii}}(P_{10}O_{32})$

The relations of these compounds will be best understood by taking as our first starting-point an assumed ortho compound, H_5O_4P, in which the atoms of phosphorus are united to hydroxyl by all their five affinities. Common and metaphosphoric acids are now simply the successive anhydrides of this pentatomic acid. Starting next from the double molecule of our assumed compound, the following anhydrides are possible: —

	$H_{10}{}^{x}O_{10}{}^{x}P_2$	3d.	$H_4{}^{iii}O_4{}^{iii}(P{}^{v}O_3{}^{iii}P)$
1st.	$H_8{}^{viii}O_8{}^{viii}(P{}^{v}O{}^{v}P)$	4th.	$H_2{}^{v}O_2{}^{v}(P{}^{v}O_4{}^{iii}P)$
2d.	$H_6{}^{iii}O_6{}^{iii}(P{}^{v}O_2{}^{v}P)$	5th.	$(P{}^{iii}O_5{}^{iii}P)$

Of these possible compounds the second and fourth are identical with common and metaphosphoric acids, of which the symbols represent two molecules, while the third and the fifth are the pyrophosphoric acid and phosphoric anhydride of the above list. The first anhydride of this series has not yet been observed. In like manner we may take three, four, or more molecules of the first compound, and deduce from each of these condensed molecules another series of anhydrides; but of the infinite number of compounds thus possible, only the salts of the hexabasic and dodecabasic acid mentioned above are known. This scheme, however, does not include hypophosphorous and phosphorous acids, which have an anomalous constitution. They may be regarded as orthophosphoric acids in which atoms of hydroxyl (two in the first case and one in the second) have been replaced with atoms of hydrogen. The molecules of both acids contain three atoms of hydrogen, but the first is only monobasic, and the second dibasic; and this fact illustrates an important principle. In all the so-called oxygen salts, only those atoms of hydrogen are replaceable by metallic atoms which are united to the negative radical by a vinculum consisting of an equal number of *oxygen* atoms. The hydrogen and oxygen atoms thus paired are equivalent to so many atoms of the radical hydroxyl (§ 37).

335. **Phosphorous Pentoxide** is readily prepared by burning phosphorus in dry air. It is an amorphous white powder, having an intense affinity for water, and is sometimes used as a hygroscopic agent. It hisses when dropped into water, and gives a solution of metaphosphoric acid.

336. **Metaphosphoric Acid.** — This compound is obtained as a vitreous solid (glacial phosphoric acid) by heating orthophosphoric acid to redness. Its solution coagulates albumen, and one molecule of the acid saturates only one molecule of sodic hydrate. By boiling the solution the acid loses its power of coagulating albumen, and acquires greater capacity of saturation, having changed into common phosphoric acid.

337. **Common Phosphoric Acid.** — This is much the most important of these compounds. It is readily prepared by boiling phosphorus in not too strong nitric acid, and evaporating the liquid

product to the consistency of syrup. The ordinary phosphates are all salts of this acid, and one molecule of acid is capable of saturating three molecules of base. Many of the phosphates are thus constituted, and these are, theoretically (§ 39), the neutral salts; evidently we have for each base two acid salts. Thus in the case of soda we have

$$Na_3\equiv O_3\equiv PO, \qquad H,Na_2\equiv O_3\equiv PO, \qquad H_2,Na\equiv O_3\equiv PO;$$

so in the case of lime we have

$$Ca_3\equiv O_6\equiv (PO)_2, \qquad H_2,Ca_2\equiv O_6\equiv (PO)_2, \qquad H_4,Ca\equiv O_6\equiv (PO)_2.$$

Here, as in many other cases, a diatomic metal serves to solder together two molecules of the acid.

338. **Common Sodic Phosphate,** $H,Na_2\equiv O_3\equiv PO \,.\, 12\,H_2O$, is by far the most important of the salts which phosphoric acid forms with the bases previously studied. It is, moreover, the chief soluble salt of the acid, and is much used in the laboratory as a reagent. It is also highly interesting, theoretically, because it illustrates by its reactions the relations we have just been considering. A solution of the salt is neutral to test-paper, but when mixed with a solution of argentic nitrate, also perfectly neutral, we obtain a yellow precipitate of argentic phosphate, $Ag_3\equiv O_3\equiv PO$, and at the same time the solution becomes acid. If we heat some crystals of the salt to 120°, it will be found that they lose twelve molecules of water; but when the dried mass is dissolved in water, and the solution evaporated, we obtain crystals of the same form (rhombic prisms, Fig. 65) and composition as before, and which give again the same reaction. But heat some of the same crystals to a red heat, and we have a wholly different result. The salt loses thirteen molecules of water, and the residue is less soluble than before. On evaporation we obtain crystals of a different form and composition ($Na_4P_2O_7 \,.\, 10\,HO$), and the solution, after precipitation with argentic nitrate, although previously alkaline, becomes neutral. Moreover, the precipitate, instead of being yellow, is white, and has the composition $Ag_4P_2O_7$.

339. **Microcosmic Salt.** $H,NH_4,Na\equiv O_3\equiv PO \,.\, 4\,H_2O$. — If we mix together hot saturated solutions of common sodic phosphate and sal ammoniac, we obtain the following reaction: —

$$(H,Na_2\equiv O_3\equiv PO + NH_4Cl + 4\,H_2O + Aq) = H,NH_4,Na\equiv O_3\equiv PO \,.\, 4\,H_2O + (NaCl + Aq). \quad [310]$$

As the solution cools, the microcosmic salt crystallizes out, leaving sodic

chloride in solution. This salt, when ignited, loses both water and ammonia, and the sodic metaphosphate, which remains, fuses into a colorless glass at a red heat. This glass acts very much like borax, and is used in the same way as a blowpipe flux.

340. **Phosphorus and Hydrogen.** — When phosphorus is boiled with strong potash or soda lye, or with milk of lime, a gas is evolved, called phosphuretted hydrogen, which on coming in contact with the air inflames spontaneously. This gas consists almost entirely of the compound H_3P; and when soda is used the reaction by which it is formed is as follows: —

$$P_4 + (3\,Na\text{-}O\text{-}H + 3\,H_2O + Aq) = (3\,Na\text{-}O\text{-}POH_2 + Aq) + H_3P. \quad [311]$$

This crude product, however, is not pure H_3P; for when it is passed through a tube cooled by a freezing mixture it deposits a small amount of a very volatile yellow liquid, which has been found to be a second compound of phosphorus and hydrogen, H_4P_2, and has the property of inflaming spontaneously to a high degree. Moreover, the *gas* thus treated loses its power of self-lighting, and this quality in the crude product is evidently due to a small admixture of the liquid substance. When exposed to the direct sunlight, the liquid compound gives off H_3P, and deposits a yellow solid, which is a third compound of phosphorus and hydrogen, H_2P_4.

$$5\,H_4P_2 = H_2P_4 + 6\,H_3P. \quad [312]$$

This same solid compound is deposited on the sides of the vessel when the crude product first mentioned is exposed to the sunlight, and in this case also the gas loses its self-lighting power.

There are, then, three distinct compounds of hydrogen and phosphorus. But of these the first is by far the most important, and the other two are chiefly interesting as explaining the singular phenomena just noticed. The compound H_3P, called usually *phosphine*, is the analogue of ammonia gas, and differs from it in composition only in containing in the place of nitrogen the next element of the same chemical series. But the differences in properties are so great that to superficial observation it would seem as if there were no similarity between the two compounds. Thus phosphuretted hydrogen is insoluble in water, except to a very slight degree, and does not unite with any of the common acids. A more careful study, however, discovers

very marked resemblances, for it appears that H_3P does unite with HBr and HI to form the compounds $(H_4P)Br$ and $(H_4P)I$, which resemble $(H_4N)Br$ and $(H_4N)I$. Moreover, the atoms of hydrogen in H_3P may be replaced with methyl, CH_3, ethyl, C_2H_5, and other radicals yielding compounds similar to the tertiary amines, which we call in general the phosphines; and it further appears that the phosphines have a strong basic character, combining with all the ordinary acids to form a class of salts corresponding to those of the compound ammonias, and yielding also, by reactions similar to [307] and [308], compounds analogous to the hydrates of the ammonium radicals. There are, however, even here, differences to be noted, — quite important, because they point to a tendency in the series which develops into a marked character in the next element, arsenic. The compounds trimethylphosphine, $(CH_3)_3P$, and triethylphosphine, $(C_2H_5)_3P$, not only combine with acids, but they also unite, as diatomic radicals, either with two atoms of chlorine, bromine, or iodine, or with one atom of sulphur or of oxygen. Thus are formed the crystalline compounds

$$(C_2H_5)_3P{=}Cl_2, \qquad (C_2H_5)_3P{=}O, \qquad (C_2H_5)_3P{=}S.$$

Lastly, a compound has been described corresponding to liquid phosphuretted hydrogen, and having the symbol $(CH_3)_2P{-}(CH_2)_2P$, which, like the former, is both liquid and spontaneously inflammable. It has, moreover, the properties of a feeble basic radical, and in the chemical series finds its analogue on one side in the radical amidogen, and on the other in the remarkable compound kakodyl (§ 349).

341. **Phosphorus and Chlorine.** — Phosphorus combines with chlorine in two proportions. When the phosphorus is in excess, phosphorous chloride, PCl_3, is formed, which is a fuming, colorless liquid. When, on the other hand, the chlorine is in excess, we obtain phosphoric chloride, PCl_5, a white crystalline solid. Both compounds are decomposed by water, and when the water is in large excess the reactions are as follows: —

$$PCl_3 + (3\,H_2O + Aq) = (H_3{=}O_3{=}POH + 3\,HCl + Aq). \qquad [313]$$

$$PCl_5 + (4\,H_2O + Aq) = (H_3{=}O_3{=}PO + 5\,HCl + Aq). \qquad [314]$$

If in the last reaction water is not present in sufficient quantity, we obtain quite a different result.

$$PCl_5 + H_2O = PCl_3O + 2\,HCl. \qquad [315]$$

The first of the three reactions is important, because it gives an easy method of preparing phosphorous acid, and the last has a special interest, because it illustrates a valuable application of phosphoric chloride. This reagent gives us the means of replacing an atom of oxygen with two atoms of chlorine, and this simple change frequently gives a clue to the molecular constitution of a chemical compound. The compound PCl_3O is called phosphoric oxychloride, and there is also a phosphoric sulphochloride, PCl_3S. Both are fuming, colorless liquids. The last, when heated with a solution of caustic soda, gives the following remarkable reaction :—

$$(PCl_3S + 6\,Na\text{-}O\text{-}H + Aq) = (Na_3{\equiv}O_3{\equiv}PS + 3\,NaCl + 3\,H_2O + Aq). \quad [316]$$

342. **ARSENIC.** $As = 75$. — Trivalent or quinquivalent. One of the less abundant elements, but in minute quantities quite widely distributed. Found native, and in combination both with sulphur and with many of the metals. The most abundant of the native compounds is Mispickel, $FeS_2 . FeAs_2$, and by simply heating this mineral in a closed vessel the elementary substance is easily obtained.

$$2\,Fe_2As_2S_2 = 4\,FeS + As_4. \quad [317]$$

It is also prepared by subliming a mixture of arsenious oxide and charcoal.

$$2\,As_2O_3 + 3\,C = As_4 + 3\,CO_2. \quad [318]$$

343. "**Metallic Arsenic,**" As_4, has a bright, steel-gray lustre, and conducts electricity with readiness. It is therefore frequently classed among the metals, and hence called *metallic* arsenic, to distinguish it from *white* arsenic. On the other hand, it is very brittle, and closely allied in all its chemical relations to the class of elements with which it is here grouped. Arsenic, like phosphorus, is dimorphous, and may readily be crystallized, both in octahedrons of the first system and in rhombohedrons of the third. Corresponding to these two forms are two allotropic modifications, distinguished also by differences of density and of other physical qualities, although these differences are not so marked as those between the two states of phosphorus. In its ordinary condition, arsenic, when heated out of contact with the air, begins to volatilize at about 130° without previously melting, and it cannot be brought into the liquid condition except under pressure.

The *Sp. Gr.* of the solid is 5.75, and that of the vapor referred to air 10.6. Heated in contact with the air, it burns with a pale blue flame, and the product of the combustion is arsenious oxide, As_2O_3. It cannot, however, maintain its own combustion, and goes out unless the temperature is kept above the point of ignition by external means. At the ordinary temperature it rapidly tarnishes in the air, and, when in large bulk, the oxidation is sometimes sufficiently rapid to ignite the mass. Serious accidents have originated from this cause. The burning of arsenic is attended with a peculiar odor resembling garlic, which is very characteristic. It is insoluble in water or any of the ordinary solvents.

344. **Arsenic and Oxygen. — Arsenious Oxide.** As_2O_3. — The white powder which is formed by the burning of arsenic is the most important and the best known of the compounds of this element. It is obtained in very large quantities as a secondary product in the roasting of many metallic ores. Like arsenic itself, this compound is dimorphous, and may be obtained crystallized, both in octahedrons of the first system and in rhombic prisms of the fourth. Moreover, when freshly sublimed, it appears as a vitreous solid, and in this third state it is three times as soluble in water as in the crystalline condition. Common white arsenic is only sparingly soluble in water, but by continuous boiling with water this crystalline condition is changed into the vitreous (or colloidal) modification, and a much larger amount enters into solution. This change, however, is not permanent, and after long standing the excess before dissolved is all deposited in octahedral crystals. When digested with the mineral acids, or with aqua ammonia, white arsenic dissolves still more readily than in water, but on standing, the larger part of the As_2O_3 is deposited from these solutions in octahedral crystals as before, and by evaporation the whole may be thus recovered, indicating that no stable compound had been formed.

345. **Arsenites.** — Arsenious acid, $H_3{}^3O_3{}^3As$, is only known in solution; and indeed there is no evidence that As_2O_3 forms with water a definite hydrate. There are, however, several well-defined arsenites.

Potassic Arsenite (Fowler's Solution),	$H_2.K^1O_3{}^1As$
Cupric Arsenite (Scheele's Green),	$H_2Cu^2O_3{}^1As$
Argentic Arsenite (Brilliant Yellow),	$Ag_3{}^1O_3{}^1As$

The first is obtained by adding to a solution of caustic potash an excess of As_2O_3, and the last two are precipitated when a solution of

the first is added to the solution of a silver or copper salt. Arsenious anhydride is a most violent mineral poison. It is also a powerful antiseptic, and is much used in packing hides and for preserving anatomical preparations.

346. **Arsenic Acid,** $H_3{}^{\equiv}O_3{}^{\equiv}AsO$, is readily obtained by treating As_2O_3 with nitric acid.

$$As_2O_3 + 2\,H\text{-}O\text{-}NO_2 + 2\,H_2O = 2\,H_3{}^{\equiv}O_3{}^{\equiv}AsO + N_2O_3. \quad [319]$$

On evaporating the resulting solution under regulated conditions of temperature, definite hydrates, all white solids, may be obtained corresponding to the three conditions of phosphoric acid. But they differ from the latter in that when dissolved in water they all yield solutions having the same properties and containing the same tribasic acid. From this acid a large number of arseniates may be prepared. The following, all of which may be obtained in well-defined crystals, are isomorphous with the corresponding phosphates: —

$$\begin{array}{ll} Na_3{}^{\equiv}O_3{}^{\equiv}AsO\,.\,12\,H_2O & H,Na_2{}^{\equiv}O_3{}^{\equiv}AsO\,.\,12\,H_2O \\ H_2,Na^{\equiv}O_3{}^{\equiv}AsO\,.\,H_2O & H_2,K^{\equiv}O_3{}^{\equiv}AsO \end{array} \quad [320]$$

These salts may be all rendered anhydrous by heat, and from the acid salts products may be thus obtained corresponding in composition to the meta- and pyro-phosphates; but when dissolved they reunite with water and become tribasic. Hence aqueous solutions of all these arseniates give, with argentic nitrate, the same precipitate, $Ag_3{}^{\equiv}O_3{}^{\equiv}AsO$. This precipitate has a brick-red color, and enables us to distinguish an arseniate from an arsenite. It is not formed, however, if an excess of ammonia or if a free acid is present. On adding a solution of magnesic sulphate containing an excess of ammonia to a solution of an arseniate, a precipitate is obtained, $(H_4N),Mg^{\equiv}O_3{}^{\equiv}AsO\,.\,6\,H_2O$, which very closely resembles the corresponding precipitate obtained with a phosphate under the same conditions.

347. **Arsenic Anhydride,** As_2O_5, is obtained as a white amorphous solid when arsenic acid is heated nearly to redness. At a higher temperature it fuses, and is decomposed into As_2O_3 and $O=O$.

348. **Arsenic and Hydrogen.** — There are two compounds, a solid, H_4As_2, and a gas, H_3As. The gas, often called *Arsine*, is formed whenever hydrogen, in its nascent condition, comes in contact with a compound of arsenic, and its formation gives us one of the most delicate means of detecting the presence of arsenic in cases of poisoning. Thus,

when arsenious acid is introduced into an apparatus evolving hydrogen, we have the reaction

$$H_3^{\equiv}O_3^{\equiv}As + 3\,H\text{-}H = 3\,H_2O + H_3As. \qquad [321]$$

As thus obtained, however, the gas is more or less mixed with hydrogen. It may be obtained pure by the following reaction : —

$$Sn_3As_2 + (6\,HCl + Aq) = (3\,SnCl_2 + Aq) + 2\,H_3As. \qquad [322]$$

It is a colorless gas (Sp. Gr. 33.9), which may be condensed to a liquid boiling at 30°. It has a repulsive odor, and is exceedingly poisonous. It burns in the air, forming As_2O_3 and H_2O, and the flame deposits on a cold surface, which is pressed upon it, a brilliant mirror of metallic arsenic. The gas is decomposed when passed through a red-hot glass tube, and a similar mirror is formed on the inner surface in front of the heated portion. By careful experimenting these mirrors may be obtained with hydrogen gas which contains only a mere trace of arsenic. When arseniuretted hydrogen is passed into a solution of argentic nitrate, we obtain the following remarkable reaction : —

$$H_3As + 6\,Ag\text{-}O\text{-}NO_2 + 3\,H_2O = 3\,Ag_2 + 6\,H\text{-}O\text{-}NO_2 + H_3^{\equiv}O_3^{\equiv}As.$$

When passed into strong nitric acid, —

$$3\,H_3As + 8\,HNO_3 = 3\,H_3^{\equiv}O_3^{\equiv}AsO + 4\,H_2O + 8\,NO, \qquad [323]$$

or,

$$H_3As + 8\,HNO_3 = H_3^{\equiv}O_3^{\equiv}AsO + 4\,H_2O + 8\,NO_2.$$

349. **Compounds with the Alcohol Radicals.** — Arsenic forms compounds analogous to the amines, phosphines, and their derivatives. The compounds trimethyl-arsine, $(CH_3)_3As$, and triethyl-arsine, $(C_2H_5)_3As$, do not, however, like the corresponding phosphines, combine directly with HCl and the similar acids, but they do unite very readily with two atoms of chlorine, bromine, or iodine, or with one atom of oxygen or sulphur, forming such compounds as

$$(CH_3)_3As\text{-}Cl_2, \qquad (C_2H_5)_3As\text{-}Br_2, \qquad (CH_3)_3As\text{-}O, \qquad (C_2H_5)_3As\text{-}S.$$

They also unite with the iodides and bromides of the alcohol radicals, forming such compounds as

$$(CH_3)_4As\text{-}I, \qquad \text{or} \qquad (C_2H_5)_4As\text{-}Br,$$

and from these may be derived basic compounds analogous to ammonic hydrate, like

$$(CH_3)_4As\text{-}O\text{-}H, \qquad \text{or} \qquad (C_2H_5)_4As\text{-}O\text{-}H.$$

But by far the most important of this class of compounds are those which may be regarded as derived from a remarkable radical substance, $(CH_3)_2As\text{-}(CH_3)_2As$, called kakodyl, which is formed when a mixture of arsenious anhydride and potassic acetate is submitted to distillation in a closed retort. A crude complex product is thus obtained, from which the radical substance may be subsequently separated. Pure kakodyl is a spontaneously inflammable, exceedingly fetid, fuming liquid, resembling in many respects the corresponding compound of phosphorus. It enters into direct combination with several of the elements, and is one of the best defined of the radical substances. Representing the group of atoms $(CH_3)_2As$ by Kd, the symbols of a few of the more characteristic compounds will be as follows: —

Kakodyl,	$Kd\text{-}Kd$
Kakodylous Oxide,	Kd_2O
Kakodylic Oxide,	Kd_2O_2
Kakodylic Acid,	$H\text{-}O\text{-}KdO$
Kakodylic Anhydride,	Kd_2O_3
Kakodylous Sulphide,	Kd_2S
Kakodylic Sulphide,	Kd_2S_2
Sulpho-kakodylic Acid,	$H\text{-}S\text{-}KdS$
Sulpho-kakodylic Anhydride,	Kd_2S_3
Kakodylous Chloride, Bromide, or Iodide,	$KdCl$, $KdBr$, or KdI
Kakodylic Chloride, Bromide, or Iodide,	$KdCl_3$, $KdBr_3$, or KdI_3

The mutual relations of the compounds studied in this section are illustrated by the following scheme, which includes all the known compounds of arsenic with methyl ($Me = CH_3$) and chlorine: —

Type H_3N.	Type ClH_4N.
$Me, Me, Me{\equiv}As$	$Cl, Me, Me, Me, Me{\equiv}As$
$Cl, Me, Me{\equiv}As$	$Cl, Cl, Me, Me, Me{\equiv}As$
$Cl, Cl, Me{\equiv}As$	$Cl, Cl, Cl, Me, Me{\equiv}As$
$Cl, Cl, Cl{\equiv}As$	$Cl, Cl, Cl, Cl, Me{\equiv}As$

By direct union with Cl_2, the compounds of the first column may be changed into the compounds of the second column on the next

lower line, and the compounds of the second column, when heated, break up into $MeCl$ and the corresponding compound of the first column on the same line. Moreover, the first compound of the first column unites directly with $MeCl$ to form the first compound of the second column. Besides the compounds mentioned above, this scheme includes another class of compounds, which may be regarded as formed from the radical $(CH_3)As$ (corresponding to HN), not yet isolated. Such are

$(CH_3)As{=}I_2$, $(CH_3)As{=}O$,
$(CH_3)As{\equiv}Cl_4$, $H_2{=}O_2{=}((CH_3)As{=}O)$.

They are called arsenmonomethyl iodide, oxide, etc., and the last, arsenmonomethylic acid. It is evident that the quantivalence of the radical is not the same in all the compounds.

350. **Compounds with Chlorine, Bromine, and Iodine.** — These elements unite directly with arsenic, but only in one proportion, forming $AsCl_3$, $AsBr_3$, and AsI_3. The first is a liquid, the last two are volatile solids at the ordinary temperature of the air. They are all decomposed by water.

$$2\,AsBr_3 + 3\,H_2O = As_2O_3 + 6\,HBr. \qquad [324]$$

351. **Compounds with Sulphur.** — Arsenic and sulphur may be melted together in all proportions. They also form several distinct compounds. The most important are, —

352. **Realgar**, As_2S_2, a brilliant *red* solid, much used as a pigment, and found in nature well crystallized.

353. **Orpiment**, As_2S_3, a brilliant *yellow* solid, also used as a paint. Formed whenever arsenic is precipitated from its solutions by H_2S. Also found crystallized in nature. The precipitated sulphide is insoluble even in strong hydrochloric acid, but it is readily soluble in solutions of caustic alkalies; also of ammonia, ammonic sulphide, and even of ammonic carbonate. From all these solutions it is again precipitated by acids.

$$As_2S_3 + (4\,K\text{-}O\text{-}H + Aq) = (H,K_2{=}O_3{=}As + H,K_2{=}S_3{=}As + H_2O + Aq). \qquad [325]$$

$$(H,Na_2{=}O_3{=}As + 3\,H_2S + Aq) = (H,Na_2{=}S_3{=}As + 3\,H_2O + Aq). \qquad [326]$$

$$As_2S_3 + (6\,K\text{-}S\text{-}H + Aq) = (2\,K_2{=}S_3{=}As + Aq) + 3\,H_2S. \qquad [327]$$

$$(2\,K_2{=}S_3{=}As + 6\,HCl + Aq) = As_2S_3 + (6\,KCl + Aq) + 3\,H_2S. \qquad [328]$$

Compare [353 to 355] beyond.

354. **Arsenic Sulphide.** As_2S_5. — Only known in combination.

Sulphur Salts. — The sulphides As_2S_3 and As_2S_5 are "sulphur anhydrides," and form with the sulphur bases a very large and important class of sulphur salts, many of which are native compounds and important metallic ores. The reactions [325 to 328] will illustrate the formation of compounds of this class.

Sulpho-arsenites.

Proustite,	Hexagonal,	$Ag_3^{\equiv}S_3^{\equiv}As$
Tennantite,	Isometric,	$[Cu_2]_3^{\equiv\equiv}S_6^{\equiv\equiv}As_2 \,.\, FeS$
Sartorite,	Orthorhombic,	$Pb^{=}S_2^{=}As_2S_2$
Dufrénoysite,	Orthorhombic,	$Pb_2^{\equiv}S_4^{\equiv}As_2S$

Sulpho-arseniates.

Enargite,	Orthorhombic,	$[Cu_2]_3^{\equiv\equiv}S_6^{\equiv\equiv}(AsS)_2$

These symbols should be compared with those of the corresponding compounds of antimony, in connection with which their mutual relations will be explained.

355. **Characteristic Reactions.** — The importance of proving the presence or absence of arsenic in cases of suspected poisoning has led to a most careful study of the characteristic reactions of this element, and hence our knowledge on these points is unusually accurate and full. The most striking of these reactions have already been given. Further details or descriptions of methods by which arsenic, even when in minute quantities, may be detected and distinguished from antimony, lie beyond the scope of the present work.

356. **ANTIMONY.** $Sb = 120$. — Trivalent or quinquivalent. This element is less abundantly distributed than arsenic, although found in similar associations. The most abundant native compound is the gray sulphide, Antimony Glance, Sb_2S_3, which occurs not only in a pure state, but also in combination with other metallic sulphides. Antimony is sometimes, although rarely, found in the metallic state, and likewise in combination with oxygen.

357. **Metallic Antimony** is most readily extracted from the native sulphide by smelting the ore with metallic iron.

$$Sb_2S_3 + 3\,Fe = 3\,FeS + Sb_2. \qquad [329]$$

It is also extracted by first roasting the ore,

$$2\,Sb_2S_3 + 9\,O^{=}O = 2\,Sb_2O_3 + 6\,SO_2, \qquad [330]$$

and then melting with charcoal and sodic carbonate. The last operation converts into oxide the small portion of the sulphide which escaped oxidation in the roasting process,

$$Sb_2S_3 + 3\,Na_2CO_3 + 3\,C = Sb_2O_3 + 3\,Na_2S + 3\,CO_2, \quad [331]$$

and the charcoal reduces the oxide to metallic antimony,

$$Sb_2O_3 + 3C = Sb_2 + 3\,CO. \quad [332]$$

By oxidizing the crude metal with nitric acid, and again reducing with charcoal, the antimony may be obtained in a pure condition.

Antimony is closely allied to arsenic, but possesses the properties of a metal to a still higher degree. It has a bright metallic lustre, which it preserves in the air. It has a high *Sp. Gr.* (6.7), and conducts heat and electricity with facility. Its conducting power, however, is inferior to that of the perfect metals, and, moreover, it is very brittle, and may be readily reduced to powder. It has also a highly crystalline structure, and, like arsenic, it may be obtained crystallized both in rhombohedrons of the third system and in octahedrons of the first. The first is the common form, and lumps of the metal may sometimes be cleaved parallel to the rhombohedral planes, which are always more or less evident on the fractured surface. Antimony melts at 450°, and is volatilizes, but only very slowly, at a full red heat. The melted metal, when heated in the air, slowly oxidizes, and before the blowpipe it burns, the product of the oxidation being in either case Sb_2O_3. Antimony is only very slightly acted on by pure hydrochloric acid, even when concentrated and boiling; but on the addition of a very small amount of nitric acid, the metal dissolves easily, forming a solution of $SbCl_3$.

$$Sb_2 + (6\,HCl + 6\,HNO_3 + Aq) = (2\,SbCl_3 + 6\,H_2O + Aq) + 6\,NO_2 \quad [333]$$

With the aid of heat it dissolves in strong sulphuric acid.

$$Sb_2 + 6\,H_2SO_4 = Sb_2^{III}O_6^{III}(SO_4)_3 + 3\,SO_2 + 6\,H_2O. \quad [334]$$

Nitric acid, when in excess, converts the metal into a white powder insoluble in the acid (chiefly Sb_2O_4). If, however, the nitric acid contains a little hydrochloric acid, the product is metantimonic acid.

$$Sb_2 + 4\,H\text{-}O\text{-}NO_2 = 2\,H\text{-}O\text{-}SbO_2 + H_2O + N_2O_3 + 2\,NO. \quad [335]$$

Lastly, antimony dissolves readily in a mixture of tartaric and nitric acids, which is one of the best solvents of the metal. Metallic antimony is chiefly used in the arts to form alloys with other metals, to which it imparts a greater hardness and durability. Type-metal is an alloy of four parts of lead and one of antimony. This alloy expands in "setting," and therefore takes a sharp impression of the mould in which it is cast; and this property, as well as the hardness, renders type-metal peculiarly suitable to the important use to which it is applied. Britannia metal, an alloy of brass, antimony, tin, and lead, much used as the base of plated silver-ware, also owes its hardness and durability to the antimony it contains.

358. **Antimony and Chlorine.—Antimonious Chloride.** $SbCl_3$. — A solution of this compound is readily obtained, either by [333], or by dissolving the native sulphide in hydrochloric acid. On evaporating the excess of acid, and distilling the residue, the chloride is obtained as a white crystalline solid. It is deliquescent, very volatile, and melts so readily (72°) that it was formerly known as Butter of Antimony. The Sp. Gr. of its vapor, as found by experiment, is 112.7. Antimonious chloride may also be obtained by distilling antimony or antimonious sulphide with mercuric chloride, and also by distilling a mixture of antimonious sulphate with common salt.

$$Sb_4 + 4\,HgCl_2 = Sb_2Hg_2 + [Hg_2]Cl_2 + 2\,SbCl_3. \qquad [336]$$

$$Sb_2S_3 + 3\,HgCl_2 = 3\,HgS + 2\,SbCl_3. \qquad [337]$$

$$Sb_2O_3(SO_2)_3 + 6\,NaCl = 3\,Na_2SO_4 + 2\,SbCl_3. \qquad [338]$$

Antimonious chloride is decomposed by water, forming an insoluble oxychloride and hydrochloric acid. Hence the solution obtained by [333] becomes turbid when diluted with water. The presence of tartaric acid in sufficient quantity prevents the decomposition, and a solution of this acid dissolves the oxychloride when formed. By long-continued washing the oxychloride may be converted into antimonious oxide.

$$(SbCl_3 + Aq) = SbOCl + (2\,HCl + Aq). \qquad [339]$$

$$4\,SbCl_3 + Aq = Sb_4O_5Cl_2 + (10\,HCl + Aq).$$

$$Sb_4O_5Cl_2 + Aq = 2\,Sb_2O_3 + (2HCl + Aq). \qquad [340]$$

Antimonious chloride combines with the chlorides of the metals of

the alkalies and of the alkaline earths, and forms soluble crystalline salts. Hence it may be mixed with concentrated solutions of these chlorides, as also with strong hydrochloric acid, without undergoing decomposition. The following are the symbols of a few of these double chlorides, which are best regarded as molecular compounds:—

$3\,(H_4N)Cl\,.\,SbCl_3\,.\,1\tfrac{1}{2}H_2O$,* $\quad 2\,(H_4N)Cl\,.\,SbCl_3\,.\,H_2O$,
$3\,KCl\,.\,SbCl_3$, $\quad 2\,KCl\,.\,SbCl_3$,
$3\,NaCl\,.\,SbCl_3$, $\quad BaCl_2\,.\,SbCl_3\,.\,2\tfrac{1}{2}H_2O$.*

359. **Antimonic Chloride**, $SbCl_5$, may be formed by passing chlorine gas over $SbCl_3$, or by acting on the metal with an excess of the same reagent. It is a volatile, fuming liquid, which readily parts with two fifths of its chlorine, and is therefore sometimes used, like PCl_5, as a chloridizing agent. It is at once decomposed by water. With only a small quantity it forms an oxychloride (compare [315]).

$$H_2O + SbCl_5 = 2\,HCl + SbCl_3O. \qquad [341]$$

With an excess of water, meta- or dimeta-antimonic acid results.

$$SbCl_5 + 4\,H_2O = H_3{\equiv}O_3{\equiv}SbO + 5\,HCl, \qquad [342]$$

or

$$2\,SbCl_5 + 7\,H_2O = H_4{\equiv}O_4{\equiv}Sb_2O_3 + 10\,HCl. \qquad [343]$$

The presence of tartaric acid prevents these reactions. By the action of H_2S on $SbCl_5$ a sulpho-chloride may be formed.

$$SbCl_5 + H_2S = SbCl_3S + 2\,HCl. \qquad [344]$$

A bromide of antimony, $SbBr_3$, and an iodide, SbI_3, are readily formed by the direct action of these elements on the metal, but no penta-bromide or iodide has yet been obtained. They are both fusible and volatile solids, and when acted on by water are converted into $Sb_4O_5Br_2$ and $Sb_4O_5I_2$. The corresponding fluoride dissolves in water without decomposition, and forms with the alkaline fluorides a number of double salts.

$3\,NaF\,.\,SbF_3$, $\quad 2\,(H_4N)F\,.\,SbF_3$, $\quad KF\,.\,SbF_3$

360. **Antimony and Oxygen. — Antimonious Oxide.** Sb_2O_3.— This compound, already mentioned as a product of the direct oxidation of antimony, may, like As_2O_3, be obtained crystallized both in octahe-

* These symbols are thus written to show the relations of the compounds. To be strictly accurate, they should be doubled.

drons of the first system or in rhombic prisms of the fourth, and on this difference of form depends the distinction between the two minerals Senarmontite and Valentinite, both of which consist of this same substance. The oxide is most readily prepared artificially by pouring a solution of $SbCl_3$ [333] into a boiling solution of sodic carbonate.

$$(3\,Na_2{=}O_2{=}CO + 2\,SbCl_3 + Aq) = \mathbf{Sb_2O_3} + (6\,NaCl + Aq) + 3\,\mathbf{CO_2}. \quad [345]$$

Antimonious oxide acts both as a basic and as an acid anhydride, although the first is by far its most marked character. It is but very slightly soluble in water. When the solution of $SbCl_3$ is poured into a cold solution of sodic carbonate, we have the reaction,

$$(3\,Na_2{=}O_2{=}CO + 2\,SbCl_3 + H_2O + Aq) = 2\,\mathbf{H\text{-}O\text{-}SbO} + (6\,NaCl + Aq) + 3\,\mathbf{CO_2}, \quad [346]$$

and the product may be regarded as meta-antimonious acid, for it dissolves in caustic alkalies, and forms definite, although very unstable, salts. On the other hand, the oxide dissolves in fuming sulphuric and fuming nitric, as well as in hydrochloric acid, forming crystalline salts in which the antimony plays the part of a basic radical.

The most important salt of this class is that formed by dissolving Sb_2O_3 in a solution of acid potassic tartrate (Cream of Tartar). This compound is very much used in medicine as an emetic, and hence the trivial name *Tartar Emetic*. Tartaric acid is tetratomic, but only dibasic (§ 44), and we have the following series of compounds: —

Tartaric Acid,	$\overset{+}{H}_2, \bar{H}_2{=}O_4{\equiv}(C_4H_2O_2)$
Neutral Potassic Tartrate,	$K_2, \bar{H}_2{=}O_4{\equiv}(C_4H_2O_2)$
Acid Potassic Tartrate,	$K, H, \bar{H}_2{=}O_4{\equiv}(C_4H_2O_2)$
Tartar Emetic (crystallized),	$K, SbO, \bar{H}_2{=}O_4{\equiv}(C_4H_2O_2) \,.\, H_2O$
" after heating to 200°,	$K, Sb{=}O_4{\equiv}(C_4H_2O_2)$

It will be noticed that in forming tartar emetic the radical SbO of the compound $H\text{-}O\text{-}SbO$ takes the place of one atom of basic hydrogen, which still remains unreplaced in cream of tartar. On heating the crystallized salt to 100°, it gives up its water of crystallization. At 200°, it gives off an additional molecule of water, formed at the expense of the oxygen in the radical just named, and of the two atoms of hydrogen distinguished as negative in the acid; and it will be seen that, in

the anhydrous salt thus obtained, one atom of antimony takes the place of three typical atoms of hydrogen in tartaric acid. Compounds similar to tartar emetic may be made in a similar way with the oxides of arsenic, bismuth, and uranium. Their symbols differ from that of tartar emetic only in having the radicals AsO, AsO_2, BiO, or UO_2 in place of SbO, and they undergo a similar decomposition when heated. Compounds of the same class may also be obtained with other anhydrides than those of the group of elements we are now studying (Fe_2O_3, Cr_2O_3, B_2O_3, etc.), and when it is further added that the potassium in these compounds may be replaced by other univalent radicals or even by bivalent radicals soldering together two molecules of the ordinary type, it will be seen that a very large number of such salts are possible. Lastly, the fact that a compound has been prepared in which two of the typical atoms of hydrogen are replaced by the positive radical ethyl, while the other two are replaced by the negative radical acetyl, and the additional fact that no salt can be obtained in which all the four atoms are replaced by a well-defined positive radical, give a strong presumption in favor of the formulæ of the tartrates adopted above.

Antimonious oxide, when heated out of contact with the air, volatilizes unchanged; but under the same conditions in the air it burns like tinder, forming a higher oxide, Sb_2O_4, which is fixed, even at a high red heat. By ignition with charcoal or hydrogen, all the oxides are readily reduced to the metallic state.

361. **Antimonic Acid.** — The reactions have already been given [333, 342, 343], by which three conditions of this acid may be prepared. They are

Orthoantimonic Acid,	$H_3^{\text{I}}O_3^{\text{I}}Sb$
Meta-antimonic Acid,	$H_3^{\text{I}}O_4^{\text{I}}SbO$
Dimeta-antimonic Acid,	$H\text{-}O\text{-}SbO_2$
Metadiantimonic Acid,	$H_4^{\text{I}}O_4^{\text{I}}Sb_2O_5$

The last is called generally pyroantimonic acid, and may also be prepared by acidifying a solution of its acid potassic salt described below,

$$(H_2K_2^{\text{I}}O_4^{\text{I}}Sb_2O_5 + 2HCl + Aq) = H_4^{\text{I}}O_4^{\text{I}}Sb_2O_5 + (2KCl + Aq); \quad [347]$$

but when this precipitate is dried, it loses water and changes into meta-antimonic acid,

$$H_4^{\text{I}}O_4^{\text{I}}Sb_2O_5 = 2\,H\text{-}O\text{-}SbO_2 + H_2O. \quad [348]$$

The existence of orthoantimonic acid has not been as yet well established, but the others are known, and many of their salts have been investigated. The most interesting of these salts is obtained by fusing antimonic anhydride with an excess of potassic hydrate, and extracting the fused mass with water. An alkaline solution is obtained, containing a salt whose composition is expressed by the symbol $H_2,K_2\equiv O_4\equiv Sb_2O_5$. This solution produces a precipitate in solutions of salts of sodium, and is sometimes used as a reagent in testing for this element. The sodic salt thus precipitated has the composition $H_2,Na_2\equiv O_4\equiv Sb_2O_5 . 6\,H_2O$. Antimonic acid, in either of its conditions, is insoluble in water, as are also the antimoniates, with a few exceptions. In this respect they frequently differ from the corresponding compounds of phosphorus and arsenic, which they closely resemble in molecular constitution.

362. **Antimonic Anhydride,** Sb_2O_5, is readily prepared by gently heating meta-antimonic acid, the product of reaction [335]. It is a pale yellow powder, insoluble in water. Fused with alkaline hydrates or carbonates, it yields various antimoniates. When ignited alone it gives off one fifth of its oxygen, and the product is the same white powder, Sb_2O_4, which is formed by the oxidation of antimonious oxide. This intermediate oxide is the most stable of the oxides of antimony. It is sometimes called antimonious acid, and when fused with the alkalies it enters into combination with them; but the products thus obtained may be regarded as mixtures of an antimonite and an antimoniate, and the oxide itself appears to be an antimoniate of antimony, $SbO\text{-}O\text{-}SbO_2$. A rare mineral called Cervantite has the same composition.

363. **Antimony and Hydrogen. — Stibine, or Antimoniuretted Hydrogen.** H_3Sb. — When any soluble compound of antimony is added to an apparatus evolving hydrogen [64], we obtain a product closely resembling arseniuretted hydrogen, but containing antimony instead of arsenic.

$$SbCl_3 + 3\,H\text{-}H = H_3Sb + 3\,HCl. \qquad [349]$$

The antimony compound thus formed is always mixed with much hydrogen gas, and has not yet been obtained in a pure condition. When burnt in air it yields water and antimonious oxide.

$$2\,H_3Sb + 3\,O\text{=}O = Sb_2O_3 + 3\,H_2O. \qquad [350]$$

If burnt against a cold surface, so that the combustion is incomplete, the antimony is deposited and a metallic mirror is formed.

$$4(C_2H_5)_3Sb + 3H_2O = Sb_4O_3 + 6C_2H_6 \qquad [357]$$

The compound is decomposed, and a similar mirror formed when its gas is passed through a red-hot tube.

When the gas is transmitted through a solution of cupric nitrate, we get the reaction

$$(C_2H_5)_3Sb + 4Cu(NO_3)_2 + 4H_2O = Sb(OH)_5 + (C_2H_5)_3SbO(NO_3)_2 + 4HNO_3. \qquad [358]$$

This reaction, and the well-established trivalent character of antimony, for the composition of antimoniuretted hydrogen beyond all reasonable doubt.

Compounds of antimony with the alcohol radicals have been prepared, both after the type of ammonia and that of the ammonium salts. Thus we have,—

Trimethyl-stibine,	$(CH_3)_3Sb$
Trimethyl-stibine Chloride,	$(CH_3)_3SbCl_2$
Trimethyl-stibine Oxide,	$(CH_3)_3SbO$
Tetramethyl-stibonium Iodide,	$(CH_3)_4SbI$
Tetramethyl-stibonium Hydrate,	$(CH_3)_4Sb{-}O{-}H$

and the corresponding compounds of ethyl and amyl. The reaction of triethyl-stibine on hydrochloric acid is interesting, as it illustrates the serial relations among the group of elements we are studying. $(C_2H_5)_3Sb$ does not combine with HCl, but actually decomposes the acid, yielding $(C_2H_5)_3SbCl_2$ and $H{-}H$. Compounds of antimony corresponding to those of the kakodyl group are not known.

364. **Antimony and Zinc.**—There are two very well marked crystalline compounds of antimony and zinc, Zn_3Sb_2 and Zn_2Sb_2, which give still further evidence of the usual trivalent character of antimony. The compound Zn_2Sb_2, moreover, decomposes water with the evolution of hydrogen gas.

365. **Antimony and Sulphur (Crude Antimony).—Antimonious Sulphide.** Sb_2S_3.—The gray sulphide of antimony has already been noticed as a native product. It is known to mineralogists as Antimony Glance, or Stibnite, and is distinguished by its great fusibility. Large splinters of the mineral readily melt in a candle flame. Hence it is easily separated by fusion from the gangue with which it is found associated, and the process is termed "liquation." Its crystals have a bright metallic lustre, and the form of rhombic prisms of the fourth system; but a strong tendency to longitudinal cleavage gives to them a bladed appearance.

When antimony and sulphur, or antimonious oxide and sulphur, are melted together in proper proportions, a compound is obtained similar to the native sulphide. Moreover, a precipitate of the same composition falls when H_2S is passed through the solution of any antimonious compound. This precipitate, however, has a *brick-red color*, and is probably an isomeric modification of the native gray compound. It is insoluble in dilute hydrochloric acid when cold, but readily dissolves in the hot acid if moderately concentrated. It is also soluble in solutions of alkaline hydrates.

$$Sb_2S_3 + (6\,K\text{-}O\text{-}H + Aq) = (K_3^{\equiv}S_3^{\equiv}Sb + K_3^{\equiv}O_3^{\equiv}Sb + 3\,H_2O + Aq). \quad [353]$$

From this solution it is again precipitated on the addition of an acid.

$$(K_3^{\equiv}S_3^{\equiv}Sb + K_3^{\equiv}O_3^{\equiv}Sb + 6\,HCl + Aq) = Sb_2S_3 + (6\,KCl + 3\,H_2O + Aq). \quad [354]$$

In like manner it dissolves in solutions of alkaline sulpho-hydrates.

$$Sb_2S_3 + (6\,K\text{-}S\text{-}H + Aq) = (2\,K_3^{\equiv}S_3^{\equiv}Sb + Aq) + 3\,H_2S. \quad [355]$$

Antimonious sulphide is a strong sulpho-anhydride, and many of its salts are important minerals. The following are a few examples. We give the symbols in their simplest form, but in the minerals themselves the antimony is frequently more or less replaced by arsenic, and the principal metallic radical by others isomorphous with it. These compounds are best classified by referring them to a series of assumed sulphur acids, related to each other like the successive anhydrides of the oxygen acids (§ 131), but derived from the normal compound of the series by eliminating successive molecules of H_2S. They may be distinguished as ortho-, meta-, and dimeta-sulphantimonites; but these terms have no special appropriateness except so far as they imply a distinction analogous to that which obtains between similar oxygen compounds.

Ortho-sulphantimonites.

Pyrargyrite,	Hexagonal,	$Ag_3^{\equiv}S_3^{\equiv}Sb$
Stephanite,	Orthorhombic,	$Ag_3^{\equiv}S_3^{\equiv}Sb\,.\,Ag_2S$
Polybasite	Orthorhombic,	$Ag_3^{\equiv}S_3^{\equiv}Sb\,.\,3\,Ag_2S$
Bournonite,	Orthorhombic,	$[Cu_2], Pb_2^{\equiv}S_6^{\equiv}Sb_2$
Meneghinite,	Monoclinic,	$Pb_3^{\equiv}S_6^{\equiv}Sb_2\,.\,PbS$
Tetrahedrite,	Isometric,	$[Cu_2]_3^{\equiv}S_6^{\equiv}Sb_2\,.\,ZnS$

Meta-sulphantimonites.

Miargyrite,	Monoclinic,	$Ag''S''SbS$
Zinkenite,	Orthorhombic,	$Pb''S_2''Sb_2S_3$
Chalcostibite,	Orthorhombic,	$Cu''S_2''Sb_2S_3$
Berthierite,		$Fe''S_2''Sb_2S_3$

Sulpho-diantimonites.

Jamesonite (Feather Ore), Orthorhombic, $Pb_2'''S_4'''Sb_2S$

Freieslebenite, Monoclinic, $3\,Ag_{10}{}^{x}S_{10}{}^{x}Sb_4S\,.\,4\,Pb_5{}^{x}S_{10}{}^{x}Sb_4S$

A few points in connection with the above formulæ require further explanation. Of the three dyad atoms which compose the basic radical of the mineral Bournonite, two are atoms of lead and one a double atom of copper. Now we may either suppose that each molecule of the mineral is constituted as our symbol would indicate, or we may regard it as a molecular aggregate of two distinct compounds, namely, $[Cu_2]_3'''S_6'''Sb_2$ and $Pb_3'''S_6'''Sb_2$, and as containing for every two molecules of the last one molecule of the first. In Freieslebenite, however, the proportions of silver and lead are such that the composition of the mineral can only be accurately expressed in the second of the two ways just indicated, and this is the general rule in the mineral kingdom. Again, the minerals Stephanite, Polybasite, Meneghinite, and Tetrahedrite may be best regarded as molecular aggregates of an orthosulphantimonite and a simple metallic sulphide, in which the last plays very much the same part as the water of crystallization in our ordinary salts.

In all the above cases the results of analysis would indicate a great constancy in the relative number of heterogeneous molecules which enter into the composition of the mineral; but in other cases no such constancy is observed, and one element is found replacing another in almost any proportion. In Tetrahedrite, for example, we frequently find the copper more or less replaced by silver or mercury, the antimony in like manner by arsenic or bismuth, and the zinc by iron. This we express by writing the symbols of the replacing elements together within the same brackets. Thus $[[Cu_2], Ag_2, Hg]$ stands for only one atom, but indicates that in the mineral the copper is more or less replaced by silver and mercury. So also the symbol $[Zn, Fe]$ represents only one atom, but indicates that the zinc is to a certain

extent replaced by iron. In its most general form the symbol of Tetrahedrite would be written, —

$$[[Cu_2],Ag_2,Hg]_3^{\equiv}S_6^{\equiv}[Sb,As,Bi]_2 \,.\, [Zn,Fe]S.$$

This symbol indicates nothing in regard to the relative proportions of the elements enclosed in the same brackets, and in fact this proportion is variable in different specimens of the same mineral; but it does show that, so far as the number of atoms is concerned, —

$$[[Cu_2]Ag_2,Hg] : [Sb,As,Bi] : [Zn,Fe] = 3 : 2 : 1.$$

It is, of course, impossible, according to our present theories, that each molecule should have this complex constitution; but we may suppose that in the mineral there are certain molecules containing one set of elements, and other molecules a different set, the actual specimen being an aggregate of all; and, further, we must suppose that there are two kinds of molecular aggregation, one in which the molecules are united in more or less definite proportions, and a second where they are merely mixed in any proportions which accident may have determined.

366. **Antimonic Sulphide.** Sb_2S_5. — When H_2S is passed through a solution of $SbCl_5$, an orange-colored precipitate is formed, having the composition which our symbol indicates. It may be questioned, however, whether the precipitate is not an intimate mixture of Sb_2S_3 and $S^{\equiv}S$, for when treated with sulphide of carbon two fifths of the sulphur is dissolved, Sb_2S_3 being left; and, moreover, it is decomposed by boiling hydrochloric acid into $SbCl_3$, H_2S, and $S^{\equiv}S$. On the other hand, it is dissolved in alkaline hydrates and sulphides, forming sulphantimoniates, and from these solutions the same substance is again precipitated on the addition of an acid.

$$4\,Sb_2S_5 + (24\,K\text{-}O\text{-}H + Aq) = (3\,K_3^{\equiv}O_8^{\equiv}SbO + 5\,K_3^{\equiv}S_3^{\equiv}SbS + 12\,H_2O + Aq). \quad [356]$$

$$Sb_2S_5 + (3\,K_2S + Aq) = (2\,K_3^{\equiv}S_3^{\equiv}SbS + Aq). \quad [357]$$

$$(2\,K_3^{\equiv}S_3^{\equiv}SbS + 6\,HCl + Aq) = Sb_2S_5 + (6\,KCl + Aq) + 3\,H_2S. \quad [358]$$

367. **Characteristic Reactions.** — The formation of the red sulphide by the action of H_2S is one of the most characteristic indications of the presence of antimony; but, before this test can be applied, the antimony must be separated from all those elements which would

obscure the reaction, by the well-known methods of qualitative analysis. The blowpipe reactions of antimony are also very characteristic. They consist in the formation of a brittle metallic bead, or a coating of volatile oxide, on charcoal, and in the peculiar bluish-green color which this oxide imparts to the blowpipe flame.

368. **BISMUTH.** $Bi = 210$. — Trivalent and quinquivalent. One of the rarer elements. Usually found native, sometimes combined with sulphur, in Bismuth Glance, Bi_2S_3, and rarely with both sulphur and tellurium, in Tetradymite, Bi_2Te_2S. Metallic bismuth is readily extracted from the native mineral by fusion (liquation). After the analogy of phosphorus and arsenic, we assign to the elementary substance the molecular formula Bi_4; but since the metal does not volatilize except at a very high temperature, we have not been able to determine its molecular weight experimentally. Bismuth melts at 265°, and forms alloys which are remarkable for their great fusibility. An alloy containing two parts of bismuth, one of lead, and one of tin melts at about 94°, and the addition of cadmium reduces the melting point still lower. These alloys expand on hardening, and are, therefore, useful for making casts.

As we descend in the series from antimony to bismuth, the metallic qualities become still more marked. The *Sp. Gr.* of bismuth equals 9.83. Its lustre is brilliant, with a reddish tinge. It is less brittle than antimony, and is even slightly malleable. Bismuth may readily be crystallized in rhombohedrons isomorphous with those of antimony; but it has not yet been crystallized in forms of the isometric system. Bismuth is not dissolved by strong hydrochloric acid, nor even by sulphuric acid, except when concentrated and boiling. Nitric acid readily dissolves it with evolution of NO_2, forming a well-crystallized nitrate (distinction from antimony). The metal also dissolves in aqua-regia, and combines directly with chlorine, bromine, and iodine.

369. **Bismuth and the Alcohol Radicals.** — No compound of bismuth and hydrogen is known, but bismuth combines with ethyl, forming a very unstable liquid, which inflames spontaneously in the air, and explodes at 150°. It has the composition $(C_2H_5)_3Bi$, and from it may be obtained the compound $(C_2H_5)_3BiI_2$ in yellow six-sided crystalline plates. This is the iodide of a bivalent radical, which forms also definite but very unstable compounds with chlorine and oxygen, and is capable of replacing the hydrogen of nitric or sulphuric acid.

370. **Bismuth and Chlorine.** — Only one compound of bismuth and chlorine is known, $BiCl_3$, and this may be obtained either by passing chlorine over the metal, by distilling the metal with corrosive sublimate, or by distilling the residue obtained when a solution of the metal in aqua regia is evaporated to dryness. The product in either case is a very fusible and volatile solid, resembling the corresponding compound of antimony. It dissolves in hydrochloric acid, but is decomposed by water into hydrochloric acid and insoluble oxichloride of bismuth, $BiOCl$. The same oxichloride is precipitated when a solution of bismuthous nitrate is poured into a solution of common salt. It is a brilliant white powder, known under the name of Pearl White, and much used as a cosmetic. It is insoluble in tartaric acid, ammonic sulphide, or solution of potash, and is thus distinguished from oxichloride of antimony precipitated under similar conditions. Bismuthous chloride combines with hydrochloric acid and the alkaline chlorides to form double salts, and, like $SbCl_3$, may be mixed with concentrated solutions of these compounds without undergoing decomposition.

The compounds of bismuth with bromine, iodine, and fluorine are $BiBr_3$, BiI_3, and BiF_3.

371. **Bismuth and Oxygen.** — Metallic bismuth does not tarnish in the air, but at a red heat the melted metal slowly oxidizes, and before the compound blowpipe it burns brilliantly. The product of the oxidation is Bismuthous Oxide, Bi_2O_3. The same compound is obtained by subjecting the nitrate to a *low* red heat. It is a pale yellow powder, which melts at a full red heat to a dark yellow liquid. It is insoluble in water, and will not directly combine with it; but by pouring a solution of bismuthous nitrate in dilute nitric acid into dilute aqua ammonia, or into a solution of potassic hydrate, a white hydrate of the metal is precipitated. This hydrate, when dried, has the composition $OBi\text{-}O\text{-}H$; but there are reasons for believing that the precipitate falls of the composition $Bi_2O_3{\cdot}H_2$. By a gentle heat, or by boiling with caustic alkalies, all the water is expelled, and Bi_2O_3 is left. Bismuthous oxide is a decided basic anhydride. It is dissolved by hydrochloric, nitric, and sulphuric acids, forming definite salts. Nevertheless, by fusing the oxide with sodic carbonate, an unstable compound is obtained, in which the metal is the negative radical $(Na\text{-}O\text{-}BiO)$.

By passing chlorine through a solution of $K\text{-}O\text{-}H$, holding Bi_2O_3 in

suspension, a red deposit is obtained, which is a mixture of bismuthic acid, $H\text{-}O\text{-}BiO_2$, and bismuthic anhydride, Bi_2O_5.

$$Bi_2O_3 + (4\,K\text{-}O\text{-}H + 2\,Cl\text{-}Cl + Aq) = 2\,H\text{-}O\text{-}BiO_2 + (4\,KCl + H_2O + Aq). \quad [338]$$

The two products may be separated by means of cold nitric acid, which dissolves only the anhydride. Bismuthic acid dissolves in a solution of potassic hydrate, giving a blood-red solution; but the salt obtained on evaporation is very unstable, and is decomposed by mere washing. The other compounds of the acid are little known. At a temperature of 130° the red-colored acid is resolved into water and the brown anhydride.

Bismuthic anhydride, when gently heated, changes into an intermediate oxide, Bi_2O_4, or rather into a mixture of this oxide and Bi_2O_3. If heated in a current of hydrogen, it is at once completely reduced to the lower degree of oxidation. When heated with sulphuric or nitric acid it evolves oxygen, producing bismuthous sulphate or nitrate; and when heated with hydrochloric acid it evolves chlorine, yielding bismuthous chloride.

372. **Bismuthous Nitrate,** $Bi^{III}O_3^{III}(NO_2)_3 . 5\,H_2O$, is the most important of the salts of bismuth. It forms large deliquescent crystals. It readily dissolves in water strongly acidified with nitric acid, but when mixed with a large volume of water it is decomposed, and a white basic salt of somewhat variable composition, formerly called the Magistery of Bismuth, is precipitated. The first precipitate appears to consist mainly of the compound $Bi^{III}O_3^{III}(NO_2)_3H_2$; but this is more or less decomposed by the subsequent washings. The product is now generally known as the Subnitrate of Bismuth, and is used medicinally.

373. **Bismuthous Sulphate.**—When bismuthous oxide dissolves in sulphuric acid, the normal sulphate $Bi_2^{III}O_6^{III}(SO_2)_3$ is undoubtedly formed; but when the solution is evaporated, this salt loses the larger part of its acid, and the yellow product obtained, when the residue is gently heated, has, approximately at least, the composition $(BiO)_2{}^{III}O_2^{III}SO_2$, although, being easily decomposed by heat, it is difficult to obtain the compound in a pure condition. The formula of the basic nitrate may also be written $OBi\text{-}O\text{-}NO_2 . H_2O$, and the formation of salts of this type is characteristic of the class of elements we are studying.

374. **Bismuth and Sulphur.**—The native compound of bismuth

and sulphur already mentioned, Bi_2S_3, is isomorphous with Antimony Glance, Sb_2S_3, which it closely resembles. The same compound may be obtained by fusing bismuth with sulphur in proper proportions, and also by passing H_2S through the solution of a bismuth salt. The precipitated sulphide is black, and is not dissolved by alkaline hydrates or sulpho-hydrates. It is also insoluble in all the mineral acids when dilute. It dissolves, however, in common nitric acid when hot. But if the resulting solution is mixed with water, most of the bismuth is again precipitated as basic nitrate. When heated in the air, Bi_2S_3 is oxidized, and yields SO_2 and Bi_2O_3, which melt to dark yellow globules. Bismuthous sulphide is a sulpho-anhydride, and the following minerals may be regarded as sulpho-bismuthites : —

Kobellite,	Orthorhombic ?	$Pb_2^{\equiv}S_6^{\equiv}Bi,Sb$
Needle Ore,	"	$([Cu_2],Pb_2)^{\equiv}S_6^{\equiv}Bi_2$
Wittichenite,	"	$[Cu_2]_3^{\equiv}S_6^{\equiv}Bi_2$
Emplectite	"	$[Cu_2]^{=}S_2^{=}Bi_2S_2$

375. **Characteristic Reactions.** — The decomposition of the soluble salts of bismuth by water, with the formation of an insoluble basic salt, is the most characteristic reaction of this metal. The salts of bismuth are easily reduced on charcoal before the blowpipe, and yield a metallic bead, surrounded by a yellow coating of oxide.

QUESTIONS AND PROBLEMS.

Nitrogen.

1. In order to determine the composition of the air, 863.7 $\overline{\text{c. m.}}^3$ of air measured under a pressure of 55.76 c. m., and at 5°.5, were mixed in a eudiometer tube with a quantity of pure hydrogen. After addition of hydrogen the volume measured 1006.7 $\overline{\text{c. m.}}^3$, under a pressure of 69.11 c. m. The mixture was next exploded by an electric spark, and after the explosion the residual gas measured 800.7 $\overline{\text{c. m.}}^3$, under a pressure of 49.14 c. m., and at 5°.6. Required the composition of air by volume in 100 parts.

Solution. By [11] it will be found that the three volumes given above would have measured, under the normal conditions, respectively 621.20, 897.38, and 507.38. The absorption due to the combustion of the hydrogen is then $897.3 - 507.3 = 390$ $\overline{\text{c. m.}}^3$ Of this $\frac{1}{3}$, or 130 $\overline{\text{c. m.}}^3$, was oxygen. Hence 621.20 $\overline{\text{c. m.}}^3$ of air contained 130 $\overline{\text{c. m.}}^3$ of oxygen and 491.2 $\overline{\text{c. m.}}^3$ of nitrogen, or 100 parts contained 20.92 oxygen and 79.08 nitrogen.

2. In another experiment 885.4 c. m.³ of air, at 53.88 c. m. and 0°.5, was taken. After addition of hydrogen, the volume measured 1052.7 c. m.³, at 70.31 c. m. and 0°.5. After explosion, the volume was reduced to 858.3 c. m.³, at 51.36 c. m. and 0°.5. Required the composition of air by volume in 100 parts. Ans. Oxygen 20.93, Nitrogen 79.07.

3. One cubic metre of dry air, measured under normal conditions, was passed over ignited copper turnings. How much must the copper have increased in weight? Ans. 299.9 grammes.

4. In preparing nitrogen gas by [263], what volume of nitrogen is obtained for every litre of chlorine used? Ans. ⅓ of a litre.

5. What weight of nitric acid, *Sp. Gr.* = 1.47, can be made from 170 kilo. of soda nitre, and what weight of sulphuric acid must be used in the process [266]? Ans. 196 kilo. of sulphuric acid, 152.4 nitric acid.

6. When, in the preparation of nitric acid, two molecules of nitre are used to each molecule of sulphuric acid, one half of the nitric acid is given off with great readiness; but to obtain the second half we must heat the materials to a much higher temperature. In the first stage of the reaction sodic bisulphate is formed, and in the second, neutral sodic sulphate. Write the two successive reactions.

7. How much sulphuric acid is required for the decomposition of 202 grammes of potassic nitrate? Ans. 294 grammes.

8. Write the reaction of nitric acid on sulphur, assuming that the products are sulphuric acid and nitric oxide.

9. Write the reaction of nitric acid on copper, assuming that the products are cupric nitrate and nitric oxide.

10. How much nitric acid (*Sp. Gr.* 1.228) is required to dissolve 127 grammes of copper? Ans. 107.6 grammes.

11. How much is required to dissolve 16.7 grammes cupric oxide? Ans. 73.21 grammes.

12. A quantity of plumbic nitrate, weighing 0.993 gramme, yields on ignition 0.669 gramme of plumbic oxide. By another determination it appears that 1.324 grammes of the same salt, ignited in a glass tube with copper turnings, yield 89.34 c. m.³ of nitrogen. Deduce the percentage composition and symbol of nitric acid, assuming that the composition of plumbic oxide and the atomic weight of lead, oxygen, and nitrogen are known. What reason have you for assuming that the acid molecule contains only one atom of hydrogen?

13. Write the reaction of nitric acid on phosphorus, assuming that phosphoric acid and one or more of the oxides of nitrogen are the products of the reaction.

14. Illustrate by means of a table the relations of the various acids and anhydrides which may be theoretically derived from orthonitric acid.

15. In nitric acid and the nitrates, what is the quantivalence of nitrogen?

16. In nitrous acid and the nitrites, what is the quantivalence of nitrogen?

17. Illustrate by means of a table the relations of the various acids and anhydrides which may be theoretically derived from orthonitrous acid.

18. Can a nitrite ever be isomeric with a nitrate? What is the essential difference between the two classes of compounds?

19. Can nitrogen monoxide be regarded as the anhydride of hyponitrous acid?

20. The **Sp. Gr.** of NO_2 vapor referred to air has been found to be 1.72. How does this value agree with the number deduced from theory?

21. With what volumes of oxygen gas must one litre of NO be mixed, to prepare respectively N_2O_3 and NO_2?

22. The Sp. Gr. of NO_2 would seem to compel us to assign to the compound the symbol we have adopted, and the same group of atoms also constantly acts as a univalent radical. Can you harmonize these facts with the theory of § 54.

23. What volume of oxygen is required to convert 3 grammes of NO (in presence of water) into nitric acid? Ans. 1674.6 $\frac{\text{c. m.}^3}{}$

24. Write the reaction of NO_2 on calcic hydrate.

25. In the preparation of NO by [280], why should you anticipate that N_2O, or even nitrogen gas, might be evolved, when the nitric acid was nearly exhausted?

26. Analyze the reaction [280], and represent the two stages by separate equations.

27. Analyze the reaction [281], and determine the amounts of the different factors which should be used in order to make 10 litres of NO gas.

28. Write the reaction when ferrous sulphate, sulphuric acid, and nitre are heated together.

29. The **Sp. Gr.** of NO referred to air is 1.038. How does this compare with the theoretical number?

30. When sodium is heated in a confined quantity of NO, the volume of the gas is reduced to one half, and the residue is found to be pure nitrogen. Assuming that the Sp. Gr. is known, show that this fact proves that the symbol we have assigned to the compound must be correct.

31. Analyze reaction [277], and show in what it differs from [264].

32. What weight and what volume of N_2O can be obtained from 240 grammes of ammonic nitrate? Ans. 132 grammes, or 66.9 litres.

33. One litre of NO will yield by [278] what volume of N_2O?
Ans. ½ litre.

34. Analyze reaction [279], and represent the two stages by separate equations.

35. What evidence is given that N_2O is less stable than NO?

36. When sodium is heated in N_2O no change of volume results, and the residue is pure nitrogen. The Sp. Gr. of N_2O is 22. Deduce from these facts the symbol of the compound.

37. What volume of gas would a litre of N_2O yield when decomposed by heat? Ans. 1½ litres.

38. What is the quantivalence of nitrogen in N_2O, and what in NO?

39. What are the relations of the oxychlorides of nitrogen to the oxides?

40. What strong reason may be adduced for doubling the symbols of two of the oxides of nitrogen? What argument can you urge in favor of the symbols adopted in this book?

41. What is the specific gravity of ammonia gas referred to air, and what referred to hydrogen? Ans. 0.591, and 8.5.

42. What would be the volume of 3.0464 grammes of ammonia gas at 273°.2 and 38 c. m.? Ans. 16 litres.

43. What weight of ammonia would be obtained from one litre of NO by reaction [290]? Ans. 0.7614 gramme.

44. Ammonia gas may also be formed by the action of metallic zinc (when in contact with platinum or iron) on a mixture of a nitrate with a solution of potash. Write the reaction [291].

45. In order to determine the amount of nitric acid present in a specimen of crude soda nitre, one gramme was treated as in the last reaction. The ammonia evolved was conducted into a solution of hydrochloric acid, and

subsequently precipitated with platinic chloride. This precipitate weighed 2.1017 grammes. What was the per cent of pure soda nitre? Ans. 80%.

46. In order to obtain 10 litres of ammonia gas, how many grammes of sal ammoniac must be taken? Ans. 23.96 grammes.

47. What volume of nitrogen would be formed by burning one litre of ammonia? Write the reaction. Ans. ½ litre.

48. When an organic substance is heated with soda lime (a mixture of caustic soda and lime), all the nitrogen present is evolved as ammonia, which may be collected in hydrochloric acid and combined with platinic chloride as above. In a given determination the weight of the precipitate thus obtained was 2.232 grammes. What was the weight of nitrogen in the compound? Ans. 0.140 gramme.

49. Deduce from the results of the eudiometric experiments described in § 317 the symbol of ammonia gas. Must we know the specific gravity in order to fix the formula definitely?

50. Show that the result of the experiment with chlorine gas confirms the formula just deduced.

51. The amides may be derived from the corresponding acids through what replacement?

52. Explain the meaning of the terms *basic* and *alcoholic*, as applied to the atoms of hydrogen.

53. The nitriles (§ 321) may be regarded as cyanides of what radicals?

54. Why should you anticipate that the imide compounds would have an acid, and the nitrile compounds a basic character?

55. Write the reactions which take place when acetic, benzoic, lactic, and oxalic acids combine with ammonia.

56. Write the reactions corresponding to [304 and 305], using the sodium instead of the ammonium salts.

57. What proof do you have that ammonium is a univalent radical?

58. What per cent of NH_3 does the platinum salt contain?

59. When aqua ammonia is added to a solution of ferric chloride, $(Fe_2)Cl_6$, ferric hydrate, $(Fe_2)Ho_6$, is precipitated. Write the reaction.

60. Write two reactions in which aqua ammonia acts like a solution of caustic soda, and two others in which it does not.

61. Write the reaction which takes place when a mixture of ammonic chloride with calcic carbonate is sublimed.

62. Write the reaction by which the sublimed carbonate when exposed to the air changes to the acid carbonate.

63. When a solution of ammonic chloride is boiled with a solution of caustic soda, ammonia gas is evolved. Write the reaction.

64. Write the symbols of the compounds formed by the union of the amines described in § 318, both with hydrochloric acid and with water.

65. Write the symbol of the ammonium base which contains the radicals phenyl, C_6H_5, amyl, C_5H_{11}, ethyl, C_2H_5, and methyl, CH_3.

66. Show what different compounds may be formed by the dehydration of the acetate, lactate, and oxalate of ammonia.

67. How much heat would be developed by the explosion of one gramme of chloride of nitrogen, and to what moving power does this correspond?

68. What inference should you draw from the heat of formation of nitrogen chloride in regard to the force which unites the atoms in the molecule of nitrogen gas?

69. Compare the heat of formation of N_2O and NO, and consider how far this explains the relative stability of the two oxides, and the reactions to which they are susceptible.

70. Does the reaction [277] conform to the principle of maximum work (§ 70, proposition second)?

71. How much heat is evolved in the reaction $NH_3 + HCl = NH_4Cl$?

Phosphorus.

72. The Sp. Gr. of phosphorus vapor has been observed to be 63.5, and according to Deville no material change is effected by a temperature of 1,040°. Moreover, the specific gravities of the vapors of the following compounds have been determined, and also the per cent of phosphorus which they contain.

	Sp. Gr.	Per cent of Phosphorus.
Phosphuretted Hydrogen,	17.1	91.18
Phosphorous Chloride,	68.4	22.55
Phosphoric Oxychloride,	76.6	20.19

Given these results of observation, show how the atomic weight of phosphorus and the molecular constitution of the elementary substance may be determined.

73. The atomic weight of phosphorus now received was found by burning a known weight of red phosphorus in perfectly dry air, and weighing the phosphoric anhydride thus formed. Assuming that one gramme of phosphorus yields 2.2903 grammes of phosphoric anhydride, what must be the atomic weight of phosphorus? How far does this experiment modify the conclusion reached in the last problem?

74. How much phosphorus can be obtained from 9.3 kilo. of pure calcic phosphate by [309]? Ans. 1.24 kilo.

75. Can you discover any connection between the difference of specific heat of the two varieties of phosphorus, and the difference of calorific power? Does the first difference wholly explain the last?

76. Show that the different varieties of phosphoric acid may be derived from the assumed pentatomic acid by successive dehydration, and make a table which shall exhibit the different possible derivatives of this compound, and assign names which will indicate their derivation.

77. Taking common phosphoric acid as the starting point, in place of the assumed pentatomic acid, show how the different varieties of phosphoric acid may be deduced.

78. What is the basicity of phosphorous and hypophosphorous acids? and what is the quantivalence of phosphorus in these compounds?

79. When either phosphorous or hypophosphorous acid is heated, it breaks up into common phosphoric acid and PH_3. Write the reaction in each case.

80. Compare together the nitrates and phosphates of the univalent and bivalent metallic radicals.

81. Write the reaction of a solution of argentic nitrate on a solution of common sodic phosphate, and show why, after precipitation, the solution must be acid.

82. Write the reaction which takes place when common sodic phosphate is heated to redness.

83. Write the reaction of a solution of argentic nitrate on a solution of sodic pyrophosphate. If the first salt is used in excess, why must the solution after the precipitation be neutral?

84. Pyrophosphoric acid may be prepared by first adding plumbic acetate to a solution of sodic pyrophosphate, when plumbic pyrophosphate is precipitated, and then decomposing this precipitate suspended in water with H_2S. The solution thus obtained evaporated *in vacuo* gives crystals of the compound. Write the reactions. Why may not the solution be evaporated by heat in the usual way?

85. Write the reaction which takes place when PH_3 burns.

86. Write the symbols of trimethyl-phosphine; tetramethyl-phosphonium hydrate; trimethyl-amyl-phosphonium iodide.

87. Write the symbols of the platinum and gold salts of tetra-ethyl-phosphonium. (§ 295.)

88. Write the symbols of triethyl-phosphine oxide and triethyl-phosphine iodide. How does the last differ from triethyl-phosphonium iodide?

89. Explain the use of PCl_5 as a reagent, and give illustrations of its peculiar action.

90. Can you devise a method by which the reaction [313] may be applied in the preparation of phosphorous acid?

91. Does the reaction [316] throw any light on the constitution of phosphoric acid?

92. What different degrees of quantivalence does phosphorus manifest in the compounds described above? Point out the examples of each condition.

93. Make a summary of the resemblances and differences between the compounds of nitrogen and those of phosphorus.

Arsenic.

94. Represent by graphic symbols the constitution of Mispickel, and show how it is possible that the double atom of sulphur should replace the double atom of arsenic.

95. What should be theoretically the specific gravity of arsenic vapor referred to air? Ans. 10.4

96. Compare together the formulæ of nitrous and arsenious acids, and point out their relations to each other. Is phosphorous acid allied to the other two?

97. Write the reactions by which cupric and argentic arsenites are formed.

98. Write the symbols of the three hydrates of arsenic acid, and give their names, following the analogy of phosphoric acid.

99. If the arseniates [320] are heated until all the water is expelled, what will be the symbols of the compounds left?

100. Write the reaction of argentic nitrate on a solution of either of the compounds. [320].

101. Write the reaction of a solution of magnesic sulphate and ammonia on a solution of either of the compounds. [320.]

102. State the differences between phosphoric and arsenic acids.

103. Write the reaction which takes place when H_3As burns, both with a sufficient and with a limited supply of oxygen.

104. How may the reactions described in (§ 348) be used to detect the presence of arsenic in a suspected liquid?

105. How could you discover the presence of the arsenic acid formed by reaction [323]?

106. State the resemblances and differences between the amines, the phosphines, and the arsines.

107. Is the quantivalence of arsenic the same in all the compounds of kakodyl?

108. In what respects does kakodyl resemble, and in what does it differ from, the corresponding compound of phosphorus?

109. Does the relation of arsenic to chlorine differ materially from the relation of phosphorus to the same element?

110. Write the reaction of H_2S on a solution of As_2O_3 in dilute hydrochloric acid.

111. Analyze the reactions [325–328], and give the names of the products which are formed.

112. What would be the chemical names of the minerals Proustite and Enargite, and what are the corresponding oxygen compounds? Define the class of compounds to which these minerals belong.

Antimony.

113. Why is the molecular weight of antimony doubtful?

114. Theoretically, what weight of metallic antimony should be obtained from 1,020 kilo. of Antimony Glance? Ans. 732 kilo.

115. The most common impurities of commercial antimony are arsenic, iron, copper, and lead. Why should the process described in § 357 tend to remove these substances?

116. Write the reaction when antimony burns.

117. Write the reaction of nitric acid on antimony, assuming that the products are Sb_2O_4 and NO.

118. Write the reaction of hydrochloric acid on Sb_2S_3. What will prevent the resulting solution from becoming turbid when mixed with water?

119. What should be theoretically the Sp. Gr. of $SbCl_3$?

120. Why is it probable that the double chlorides (§ 358) are molecular compounds?

121. When $SbCl_3$ is mixed with strong $HCl + Aq$, what compound would analogy lead us to suppose is formed in the solution?

122. Write the reaction of chlorine gas (in excess) on antimony and on $SbCl_3$.

123. Write the reaction of water on $SbBr_3$ and SbI_3.

124. Write the reactions when Sb_2O_3 dissolves in $HCl + Aq$ and H_2SO_4. [334.]

125. Write the reaction when Sb_2O_3 dissolves in cream of tartar.

126. Write the reaction when tartar emetic is heated to 200°.

127. Write the symbols of the compounds formed by dissolving As_2O_3, As_2O_5, or Bi_2O_3, in cream of tartar.

128. Write the symbols of the compounds of the same class derived from Fe_2O_3, Cr_2O_3, and B_2O_3, assuming that the radicals Fe_2O_2, Cr_2O_2, and BO replace the SbO of tartar emetic.

129. Write the reaction when to a solution of tartar emetic is added a solution of calcic chloride, knowing that the corresponding calcium compound, being insoluble, is precipitated. Calcium, it must be remembered, takes the place of two atoms of potassium.

130. Write the symbol of diaceto-diethylic tartrate.

131. State the grounds for the distinction between the three sets of hydrogen atoms which tartaric acid contains. By what names do you distinguish the different sets of atoms, and what other examples have been studied in which a similar distinction has been made?

132. What is the name of the compound $H_2K_2^1O_4^2Sb_2O_3$? Write the reaction of a solution of this reagent upon a solution of $NaCl$.

133. On boiling its solution, the acid potassic pyroantimoniate changes into a meta-antimoniate which does not precipitate soda. Write the reaction.

134. Write the reaction of $(HCl + Aq)$ on Zn_3Sb_2, assuming that the product is H_3Sb.

135. Write the symbols of the ethyl and amyl compounds of antimony, following the analogy of the methyl compounds whose symbols are given.

136. Write the reaction of triethyl-stibine on hydrochloric acid.

137. Represent by graphic symbols the constitution of Zn_3Sb_2 and Zn_2Sb_2, and give the symbols of other compounds formed after the same type.

138. Write the reaction when antimonious oxide and sulphur are melted together.

139. Write the reaction when H_2S is passed through a solution of tartar emetic.

140. Analyze reactions [353 – 355], and name the classes of compounds to which the several products belong.

141. Show by symbols the relations of the assumed sulphur acids to which the several sulphantimonites are referred.

142. Explain the distinction between a chemical compound and a molecular aggregate. What different orders of combination do the facts and the atomic theory require of us to assume in such a mineral as Tetrahedrite?

143. How are the phenomena of isomorphous substitution in the mineral kingdom to be explained in harmony with the atomic theory?

144. Write the reaction of H_2S on a solution of $SbCl_5$.

145. Write the reaction of hydrochloric acid on the precipitate obtained by the last reaction.

Bismuth.

146. Represent by graphic symbols the constitution of Bismuth Glance and Tetradymite.

147. Compare the qualities of metallic bismuth with those of the other elementary substances belonging to the same series, considering especially the crystalline form and the specific gravity.

148. Write the reaction of nitric acid on bismuth, and compare this reaction with that of nitric acid on antimony.

149. Write the reaction of aqua regia on bismuth.

150. Compare the compounds of the alcohol radicals with the different members of the nitrogen series of elements, and present the subject in a written form.

151. Write the different reactions by which $BiCl_3$ may be formed.

152. Write the reaction of water on $BiCl_3$, and the reaction when a solution of bismuthous nitrate is poured into a solution of common salt.

153. Why does the presence of a large amount of H_4NCl prevent a solution of $BiCl_3$ from becoming turbid when mixed with water?

154. Compare $BiCl_3$ with the corresponding chlorides of the same series. What inference do you draw from the fact that the compound $BiCl_5$ has not been obtained? Have any other facts been mentioned pointing to the same conclusion? What is the evidence that bismuth is ever quinquivalent?

155. Write the reaction when bismuth burns, or is more slowly oxidized.

156. Write the reaction when bismuthous nitrate is heated to a low red heat. Why in this process is it important to avoid a higher temperature?

157. Write the reaction when a solution of bismuthous nitrate (in dilute nitric acid) is poured into a solution of potassic hydrate.

158. Write the reactions when bismuthous oxide dissolves in hydrochloric, nitric, or sulphuric acid.

159. Compare the oxides and hydrates of the elements of the nitrogen series, and, by tabulating their symbols, show that their molecular constitution is analogous. Trace, also, the variation in their properties as you descend in the series.

160. Write the reaction of water on bismuthous nitrate, assuming that the basic salt whose symbol is given above, together with free nitric acid, are the resulting products.

161. If Bi_2S_3 and Sb_2S_3 are precipitated together, how may the two be separated?

162. Write the reaction when Bi_2S_3 is roasted in a current of air.

163. To which of the three classes of salts, distinguished in § 365, must the several sulpho-bismuthites be referred?

164. Compare the sulpho-salts of bismuth, antimony, and arsenic, and point out their mutual relations.

DIVISION XXIII.

376. **VANADIUM.** $V = 51.3$. — Trivalent and quinquivalent. A very rare element, discovered in 1830 in the iron ores of Taberg in Sweden. It has since been found associated with the iron and uranium ores of other localities, and more recently it has been found in considerable quantities in certain remarkable metalliferous sandstone beds occurring in the county of Cheshire in England. Vanadium is also the essential constituent of a few very rare minerals. Of these the most important is Vanadinite, which is a vanadate of lead, and so closely resembles the native phosphate and arseniate of the same metal as to leave no doubt that all three have a similar molecular constitution, and hence that vanadium is a perissad element, like phosphorus and arsenic. Thus we have the following minerals, which are all isomorphous with each other: —

Apatite,	$(Ca_5F)^{IX}O_9^{IX}(PO)_3$
Pyromorphite,	$(Pb_5Cl)^{IX}O_9^{IX}(PO)_3$
Mimetine,	$(Pb_5Cl)^{IX}O_9^{IX}(AsO)_3$
Vanadinite,	$(Pb_5Cl)^{IX}O_9^{IX}(VO)_3$

The study of the other compounds of vanadium leads to the same conclusion, and shows that the same character already noticed in bismuth and antimony is developed in this element to a still higher degree. The group of atoms VO acts as a powerful univalent or trivalent radical, and combines with chlorine or replaces hydrogen like an elementary atom, and almost all of the compounds of the element formerly known, and which can be directly prepared from the native vanadates, contain this important radical, now called Vanadyl; in fact, the radical substance $(VO)_2$, now recognized as an oxide of vanadium, was for a long time mistaken for the element itself. We have, for example, $(VO)Cl_3$, a yellow fuming volatile liquid boiling at 126°.7 with *Sp. Gr.* = 1.84 and Sp. Gr. = 88.2; also $(VO)Cl_2$ in brilliant green tabular crystals; next, $(VO)Cl$, a light brown powder; and lastly, $(VO)_2Cl$, a brownish yellow powder resembling mosaic gold. The true chlorides of vanadium can only be prepared from the metal or its nitride, and the air must be carefully excluded during the process. The following have been recently described by Roscoe: VCl_2,

a bright apple green solid in hexagonal plates, with a micaceous lustre; VCl_3, in brilliant tabular crystals, with color of peach-blossoms; and VCl_4, a dark reddish-brown volatile liquid, boiling at 154°, with Sp. Gr. at 0° = 1.858 and Sp. Gr. = 93.3. There are also compounds which may be regarded as containing the quadrivalent radical divanadyl, V_2O_2.

The oxides of vanadium are:—First, V_2O, a brown crust formed by the prolonged exposure of metallic vanadium to the air. Secondly, V_2O_2 or $VO{-}VO$, obtained as a gray metallic powder when the vapor of $VOCl_3$ mixed with hydrogen is passed over red-hot carbon. It dissolves in dilute acids with the evolution of hydrogen, and cannot be deprived of its oxygen except with the greatest difficulty. Thirdly, V_2O_3, obtained as a black powder when V_2O_5 is reduced by hydrogen at a red heat. It is insoluble in acids. Fourthly, V_2O_4, obtained in the form of blue shining crystals by allowing V_2O_3 to absorb oxygen from the air. Fifthly, V_2O_5, vanadic anhydride, a brownish red crystalline solid, fusible at a red heat, and sparingly soluble in water. The solution has a yellow color, and is strongly acid; but no definite hydrate has been described. Vanadic anhydride dissolves in concentrated sulphuric acid when boiling, giving a dark red solution. If this is diluted with fifty times its volume of water, and heated with metallic zinc, it rapidly changes color, passing through all shades of blue and green until it attains a permanent lavender tint. To each of these shades corresponds a certain degree of oxidation of the dissolved vanadium; thus, bright blue to V_2O_4, green to V_2O_3, and lavender to V_2O_2; and by using less active reducing agents the change may be arrested at any desired point. The lavender solution absorbs oxygen with such avidity as "to bleach indigo and other vegetable coloring matters as quickly as chlorine, and far more powerfully than any other known agent."

From vanadic anhydride we derive the vanadates, of which there appear to be five classes, corresponding to the phosphates.

1. Metavanadates, as in $NH_4{-}O{-}VO_3$, or $Pb''O_2''(VO_3)_2$. Descloizite.
2. Pyrovanadates, as in $Na_4''O_4''V_2O_3$, or $Pb_2''O_4''(V_2O_3)_2$. Descloizite.
3. Orthovanadates, as in $Na_3''O_3''VO \cdot 16H_2O$, or $Ca_3''O_6''(VO)_2$.
4. Tetravanadates, as in $(NH_4)_2''O_2''V_4O_9 \cdot 4H_2O$.
5. Hexvanadates,* as in $(NH_4){-}O{-}V_6O_{13} \cdot 6H_2O$.

* These names are those adopted by Roscoe, to whom we owe most of our knowledge of the vanadium compounds.

Of these salts the metavanadates are the most and the orthovanadates the least stable, the reverse of what is true in the case of the phosphates.

There are two nitrides of vanadium, VN and VN_2. The first is a black powder obtained by acting on $(VO)Cl_2$ with dry NH_3. Its composition has been determined by analysis, and it is interesting, not only as fixing the atomic weight of the metal, but also as the starting point from which the true chlorides of vanadium, and the metal itself, have been reached.

Metallic vanadium has been obtained by reducing VCl_2 with hydrogen. It is a light whitish-gray powder, which under the microscope appears as a brilliant crystalline metallic mass with a silver-white lustre. This metallic powder has a *Sp. Gr.* = 5.5, and is not magnetic. It does not volatilize or fuse when heated to redness in an atmosphere of hydrogen. It does not tarnish in the air, or decompose water at the ordinary temperatures; but when thrown into a flame, it burns with brilliant scintillations. It does not dissolve in hydrochloric acid hot or cold, and only slowly in hot sulphuric acid, but nitric acid of all strengths attacks it with violence. It is not acted upon by solutions of the caustic alkalies; but when fused with sodic hydrate, hydrogen gas is evolved, and a vanadate formed. It unites directly with chlorine gas to form VCl_4, and with nitrogen gas to form VN, and it is capable of absorbing as much as 1.3 per cent of hydrogen gas. It attacks all glass and porcelain in which it is heated, a compound of silicon and the metal being formed. It yields also an alloy with platinum, and for these reasons, as well as on account of its very great avidity (when heated) for both oxygen and nitrogen, it has been one of the most difficult of all the elements to isolate. The pentoxide is now an article of manufacture, and is used in the preparation of aniline black.

DIVISION XXIV.

377. **URANIUM.** $U = 120$. — One of the rarer elements. Always found in nature combined with oxygen, chiefly in Pitchblende, which is essentially the compound U_3O_4, and in a rare mineral called Uranite. Of the last there are two varieties: the first is a phosphate of uranium and calcium, and the second a phosphate of uranium and copper.

$$Ca,(UO)_4^{\text{IV}}O_6^{\text{IV}}(PO)_2 . 8H_2O, \quad \text{and} \quad Cu,(UO)_4^{\text{IV}}O_6^{\text{IV}}(PO)_2 . 8H_2O.$$

In many of its chemical characteristics, uranium very closely resembles vanadium. Like the last element, it forms an oxide, UO, which acts as a univalent radical, replacing hydrogen and combining directly with chlorine; and all the most important stable and characteristic compounds of uranium may be regarded as compounds of this radical. Moreover, U_2O_2, like V_2O_2, cannot be decomposed by the ordinary reducing agents, and was formerly mistaken for the metal itself. Uranyl acts both as a basic and as an acid radical. Of the uranyl compounds, the most important, besides the native phosphates already mentioned, are Uranyl Chloride, $(UO)Cl$: Uranyl Fluoride, $(UO)F$; Uranyl Hydrate, (UO)-O-H (a yellow powder); Uranyl Nitrate, (UO)-O-$NO_2 . 3H_2O$ (a beautiful yellow salt, crystallizing in long striated prisms); and Uranyl-potassic Sulphate, $K,(UO)$-O_2-$SO_2 . H_2O$; and to these may be added a number of remarkable double salts which may be formed by the union both of the chloride and the fluoride of uranyl with the chlorides or fluorides of the metals of the alkalies or alkaline earths. Indeed, these double salts are a characteristic feature of uranium, and one which becomes still more marked in the next element, columbium.

If to a solution of a uranyl salt we add ammonia, or the solution of any other alkali or alkaline earth, we obtain a yellow precipitate. This is not, however, as might have been expected, the hydrate of uranyl, but a compound of the radical with the alkali, in which uranyl acts as an acid radical. The constitution of these compounds is not well understood, but they are probably mixtures of uranyl hydrate with a compound of the form R-O-(UO). The so-called yellow uranium oxide of commerce is a hydrate thus prepared, retaining about two per cent of ammonia. All these uranyl compounds have a yellow color, and

the yellow oxide is used to communicate a beautiful and peculiar yellow to glass. Glass thus colored, and the transparent uranyl salts, are to a high degree fluorescent.

Judging from the uranyl compounds alone, we should conclude that uranium was a perissad closely allied to vanadium and the nitrogen group of elements; but there are other compounds of uranium which do not readily conform to this theory. Thus we have a chloride, UCl_2, and a series of *uranous* salts (all having a green color), in which one atom of the metal appears to combine with two atoms of chlorine, or to replace two atoms of hydrogen. These would seem, on the other hand, to indicate that uranium was an artiad element allied to iron; and the important fact that the native oxide, U_3O_4, is isomorphous with the magnetic oxide of iron, sustains this view. Uranium thus appears to stand between the nitrogen group of elements of the perissad family and the iron group of the artiad family. It belongs in a measure to both, and its compounds may be interpreted according to the one or the other plan of molecular grouping. In classing it with nitrogen, we merely follow what appear to be its normal relations; but others may reasonably entertain a different view, and further investigation is required to determine its quantivalence. Uranium thus illustrates very forcibly the remarks already made on chemical classification. (§ 119.)

Of metallic uranium but little is known. It has been obtained by decomposing the chloride UCl_2 with potassium, and appears to be a steel-white metal (*Sp. Gr.* = 18.4), which is slightly malleable, and not readily oxidized by atmospheric agents. If heated, however, it burns in the air, and dissolves in dilute acids with the evolution of hydrogen. The compounds of uranium have found but few applications in the arts. The "yellow oxide" is used, as already stated, for coloring glass, and the so-called black oxide (U_4O_5), obtained by igniting the nitrate, is employed as a black pigment in painting on porcelain. The nitrate, which is the most common soluble salt, has been thought to have some valuable qualities in photography.

QUESTIONS AND PROBLEMS.

1. State the grounds on which the conclusion in regard to the atomicity of vanadium is based, and represent by a graphic symbol the constitution of Vanadinite.

2. How does the Sp. Gr. of the vapor of vanadic oxytrichloride compare with the theoretical value?

3. It has been shown by careful analysis that the above chloride contains 61.276 per cent of chlorine. What is the atomic weight of vanadyl, and what that of vanadium? Ans. 67.29, and 51.29.

4. In order to determine the atomic weight of vanadium from vanadic anhydride, Roscoe reduced V_2O_5 by hydrogen to vanadic oxide, V_2O_3. Four experiments gave the following results: —

	Weight of V_2O_5 used.	Weight of V_2O_3 obtained.
1st.	7.7397 grammes.	6.3827 grammes.
2d.	6.5819 "	5.4296 "
3d.	5.1895 "	4.2819 "
4th.	5.0450 "	4.1614 "

Deduce the atomic weight of vanadium.

5. Berzelius assigned to vanadic anhydride the symbol VO_3, and to vanadyl chloride the symbol VCl_3. On this hypothesis he found for the atomic weight of vanadium, by the method of the last problem, the value 137 (when $O = 16$), which would be reduced to 134.74 by the more accurate determinations of Roscoe. State the reasons for believing that the true atomic weight of the element is 51.21, and that the compounds have the symbols assigned to them above. Show how far these conclusions have been proved, and point out the cause of the former error.

6. Make a table showing that the vanadates may be classed like the phosphates, or the borates. Is there not, however, a special reason for regarding Na_3O_3VO as an orthovanadate? Consider whether the relations which are so marked in the case of vanadium do not correspond to the fact that the ortho form is so generally wanting in the case of the oxygen acids.

7. State the grounds for classing uranium with vanadium, as well as the reasons which might be urged for associating it with iron, and write the rational symbols of the uranium compounds on the assumption that this element is an artiad.

DIVISION XXV.

378. **COLUMBIUM (Niobium).** $Cb = 94$. — Quinquivalent. This element forms the acid radical of Pyrochlore, Columbite, Samarskite, Euxenite, Æschynite, Fergusonite, and a few other rare minerals. They are all compounds of columbic anhydride, Cb_2O_5, with various metallic oxides, — among which those of cerium, yttrium, and their associated elements, are especially to be distinguished. The columbium, however, is almost invariably replaced to a greater or less extent by tantalum. Columbite, the most abundant of these minerals, has the symbol $[Fe,Mn]O_2([Cb,Ta]O_2)_2$. It has a black color, a submetallic lustre, and a specific gravity from 5.4 to 6.5, increasing as the proportion of tantalum increases. When finely powdered it is easily decomposed by fusion with potassic bisulphate, and on subsequently boiling the fused mass with water a white insoluble residue is obtained, which consists chiefly of Cb_2O_5, and from this the different compounds of columbium may be prepared. Of these the most characteristic are the following.

379. **Columbic Anhydride.** Cb_2O_5. — A white powder, which becomes crystalline when heated, and is afterwards insoluble in all acids. It has a *Sp. Gr.* between 4.37 and 4.53. Before ignition, and when in condition of hydrate (columbic acid?), it dissolves in strong sulphuric and in hydrofluoric acid. After boiling with strong hydrochloric acid, in which it is nearly insoluble, the product dissolves in water, and the solution treated with zinc turns blue, and finally deposits a blue-colored oxide. When a large excess of hydrochloric acid is present, the solution deposits a brown oxide under the same conditions; but the constitution of neither of these compounds is as yet known. It has been stated that oxides having the composition Cb_2O_2 and Cb_2O_4 have also been obtained. Columbic acid forms salts called Columbates, and, besides the native compounds mentioned above, we are acquainted with several potassic columbates, three of which have been obtained in well-defined crystals, but they have a very complex constitution.

380. **Columbic Chloride.** $CbCl_5$. — A yellow crystalline solid, melting at 194°, and boiling at 241°. It has been found by analysis to contain 65.28 per cent of chlorine, and the Sp. Gr. of its vapor, by experiment, is 9.6.

381. **Columbic Oxychloride.** $Cb OCl_3$. — A white solid, crystallizing in silky tufts, which volatilizes in the air at 400°, without previously melting. It contains, according to analysis, 48.9 per cent of chlorine, and the Sp. Gr. of its vapor has been found to be 7.1. Moreover, it has been recently *proved* that it contains oxygen. Both chlorides, when treated with water, yield columbic acid.

382. **Columbic Oxyfluoride.** $Cb OF_3$. — This compound is probably formed when columbic acid is dissolved in hydrofluoric acid, but it has not yet been isolated in a pure condition. The solution, however, forms definite crystalline salts with several metallic fluorides, and these are among the most important compounds of columbium. The salt $2KF.CbOF_3.H_2O$ is very readily obtained in nacreous scales, and being far more soluble than the compound of tantalum formed under the same conditions, $2KF.TaF_5$, it gives us the only useful means yet discovered of separating this element from columbium. A salt has also been formed, having the composition $2KF.CbF_5$, and isomorphous with the compound of tantalum just mentioned. It is interesting as pointing to a fluoride of columbium, CbF_5, which is not otherwise known.

The metal columbium has not with certainty been obtained. The black powder described as such by Rose is said to be the oxide Cb_2O_5.

An infusion of gall-nuts gives with *acid* solutions containing columbium a deep orange-red precipitate; and by this reaction columbium may be distinguished from tantalum, which, under the same conditions, gives a bright brown precipitate.

383. **TANTALUM.** $Ta = 182$. — This element, associated with columbium in the native columbates named above, is the chief constituent of Tantalite, Yttrotantalite, and of a few other minerals equally rare. Tantalite is isomorphous with Columbite, has the same composition, save only that the acid radical is wholly tantalum, and differs chiefly in having a higher *Sp. Gr.*, which varies from 7 to 8. Although tantalum is so closely allied to columbium, yet its compounds differ from those of this last element in several important respects. There appears to be no tendency to form oxychlorides or oxyfluorides, — at least no such compounds are known. The chloride is $TaCl_5$, a pale yellow solid, melting at 211°, boiling at 242°, and having a vapor density of 12.8. It contains by analysis 48.75 per cent of chlorine, and is decomposed by water, yielding tantalic acid. The fluoride is, in like manner, TaF_5. It forms double salts with the metallic fluorides,

the most important of which is the potassic fluotantalate, $2KF . TaF_5$, mentioned above. Tantalic anhydride, Ta_2O_5, is a white powder, insoluble in acids. It closely resembles columbic anhydride, and is prepared in a similar way from the native tantalates, but it has a higher density (*Sp. Gr.* = 7.6 to 8), and forms with the alkalies a larger number of crystallized salts. There is a hydrate (tantalic acid?), and also probably several lower oxides of the element. A solution of $TaCl_5$ in strong sulphuric acid, when diluted with water and reduced with zinc, becomes colored blue, but yields no brown oxide, as in the case of columbium. By reducing sodio-tantalic fluoride with sodium, a black powder is obtained, which has been supposed to be metallic tantalum.

QUESTIONS AND PROBLEMS.

1. Calculate the percentage composition of Columbite, on the assumption that the basic radical is wholly iron and the acid radical wholly columbium.

Ans. 21.17 FeO and 78.83 Cb_2O_5.

2. Explain the meaning of the symbol of Columbite in § 378.

3. How far do the theoretical **Sp. Gr.** of columbic chloride and oxychloride compare with the experimental results?

4. The mean of twenty analyses of the potassio-columbic oxyfluoride, $2KF . CbOF_3 . H_2O$, gave the following results. From 100 parts of the salt there were obtained by the process of analysis adopted 5.87 parts of water, 44.36 of columbic anhydride, 57.82 of potassic sulphate, and 31.72 of fluorine. Assuming that the symbol of columbic anhydride is Cb_2O_5, and estimating the per cent of oxygen by the loss, deduce the percentage composition of the compound, and its symbol.

Ans. Columbium, 31.12; Potassium, 25.92; Oxygen, 5.37; Fluorine, 31.72; Water, 5.87.

5. What would be the atomic weight of columbium if deduced from the result of the above analyses? Ans. 93.9.

6. Previous to the recent investigations of Marignac, the symbol of columbic acid was usually written CbO_3 when $O = 8$, or Cb_2O_3 when $O = 16$. What proofs have been given of the correctness of the symbol adopted in this book? What was the probable cause of the error made by the earlier investigators?

7. By what general method may tantalum be separated from columbium? How can you tell when the separation is complete?

8. What compounds of tantalum and columbium are isomorphous? What bearing has this fact have on the symbol of tantalic anhydride? Does the vapor density of tantalic chloride agree with the symbol which has been adopted? Why is there a necessary connection between the symbol of the chloride and that of the anhydride?

9. How may Tantalite be distinguished from Columbite?

10. State the resemblances and the differences between the two metals of this group of elements.

DIVISION XXVI.

384. **THE PLATINUM METALS.** — Prevailing quantivalence four. — The six metals, Ruthenium, Osmium, Rhodium, Iridium, Palladium, and Platinum, are always found in the native state, although more or less alloyed with each other. "Platinum Ore" is found in several countries, but at least nine tenths of the commercial supply comes from the Ural. It is everywhere obtained by washing alluvial material, generally in small rounded metallic grains, although masses of considerable size are occasionally found. The following analyses by Deville and Debray will give an idea of its composition: —

	Pt	*Au*	*Fe*	*Ir*	*Rh*	*Pd*	*Cu*	*Ir-Os*	*Sand.*
Choco	86.20	1.00	7.80	0.85	1.40	0.50	0.60	0.95	0.95
California	85.50	0.80	6.75	1.05	1.00	0.60	1.40	1.10	2.95
Oregon	51.45	0.85	4.30	0.40	0.65	0.15	2.15	37.30	3.00
Australia	61.40	1.20	4.55	1.10	1.85	1.80	1.10	26.00	1.20
Russia	76.40	0.40	11.70	4.30	0.30	1.40	4.10	0.50	1.40

In this ore the grains of "Native Platinum," which have a steel-gray color, are always more or less mixed with those of a distinct mineral species called "Iridosmine,"* which have usually a lighter color, and consist chiefly of iridium and osmium, alloyed with small quantities of rhodium and ruthenium. Hence from the above analyses the amounts of Iridosmine (*Ir-Os*) and sand must be subtracted in order to obtain the composition of native platinum proper.

In the old method of manufacturing platinum, the ore is treated with aqua-regia, which dissolves the platinum and the metals directly alloyed with it, but does not affect the Iridosmine, the titaniferous iron, and other resisting minerals, which are frequently mixed with the "Native Platinum." To the solution thus obtained, when brought into suitable condition, ammonic chloride is added, which precipitates all the platinum [306] as ammonio-platinic chloride. This precipitate, when ignited, leaves the metal in a pulverulent condition (Platinum Sponge), which is welded into a compact mass by heat and pressure.

* Iridosmine is frequently associated with California gold, and is separated from it at the assay offices in considerable quantities. Being heavier than gold, it sinks to the bottom of the crucible when the metal is fused.

In the new method of Deville and Debray the platinum is first united to metallic lead, which, as it does not alloy with iridosmine, separates the platinum from the chief impurities in the ore. The lead is subsequently removed by cupellation, and the crude platinum purified by melting it in a crucible of lime with a powerful oxyhydrogen flame. Indeed, an alloy of platinum with a small amount of iridium and rhodium, well adapted for chemical vessels, may be obtained directly from the ore by fusing it with the same flame on a bed of lime, using a small amount of lime as a flux. The palladium and osmium present are thus volatilized, while the copper and iron form fusible compounds with the lime.

From the "platinum residues," as they are termed, the associated metals can only be separated by refined analytical methods, and our knowledge of the chemical relations of these rare elements is still very imperfect. Necessarily, therefore, they must occupy a very subordinate place in an elementary treatise, and they are here, as elsewhere, classed together, more in consequence of their intimate association in nature and resemblances as metals, than from any well-defined chemical relationship.

385. **RUTHENIUM** ($Ru = 104.4$) is a white metal, very hard and brittle, with difficulty fusible before the oxyhydrogen blowpipe. *Sp. Gr.* when fused 11 to 11.4. It is scarcely attacked by nitro-muriatic acid, but it is easily oxidized when fused with potassic hydrate (especially if a little nitre be added), yielding potassic ruthenate, which forms with water an orange-colored solution. The pulverized metal heated in a current of air rapidly absorbs oxygen, and the oxides cannot be reduced by heat alone.

Five oxides are known: — First, RuO, which has a dark gray color and metallic lustre. It is not acted on by acids, but is reduced by hydrogen at the ordinary temperature. Secondly, Ru_2O_3, which is the product when the metal is oxidized by the air. It has a deep blue color, is also insoluble in acids, and is reduced by hydrogen, but only at a higher temperature. The corresponding hydrate, $[Ru_2]H_6$, which dissolves with yellow color in acids, but is insoluble in water or alkalies, is also known. Thirdly, RuO_2, which is a dark greenish blue powder, and forms a hydrate, $Ru^{\equiv}Ho_4$, that dissolves both in acids and alkalies. Fourthly, RuO_3, which is the assumed anhydride of the yellow ruthenate, formed when the metal is ignited with a mixture of potassic hydrate with potassic nitrate or chlorate. This

characteristic compound is decomposed, like potassic manganate, by acids, and even by organic substances. Lastly, RuO_4, which is a very volatile golden-yellow crystalline solid, melting at 58° and boiling at about 100°.

Ruthenium forms three chlorides: $RuCl_2$, which is known both as an insoluble black crystalline powder, and as forming a fine blue solution; $[Ru_2]Cl_6$, which forms yellow solutions and soluble compounds with the alkaline chlorides, as $[Ru_2]Cl_6 . 4\,KCl$; lastly, $RuCl_4$, known only in its double salts, $RuCl_4 . 2\,KCl$ and $RuCl_4 . 2\,(NH_4)Cl$, which, like the corresponding platinum salt, crystallizes in octahedrons (§ 392), but appears to be dimorphous, as it forms under certain conditions hexagonal prisms.

When H_2S is passed through a solution of the yellow chloride, it partly precipitates the ruthenium as a sulphide, but at the same time it partially reduces $[Ru_2]Cl_6$ to $RuCl_2$, which gives to the supernatant liquid a fine azure-blue color. Zinc effects the same reduction, and this reaction is very delicate and characteristic.

386. **OSMIUM** ($Os = 199.2$). — In the most compact condition in which this metal has been obtained, it has *Sp. Gr.* = 21.4, and a bluish tinge of color resembling that of zinc. It has never been fused, but it slowly volatilizes at the temperature at which ruthenium and iridium melt. When finely divided, it is oxidized by nitric acid, but in its more compact state it resists even aqua-regia. When heated in a current of air it oxidizes much more readily than ruthenium, passing at once to the highest degree of oxidation, OsO_4, and forming a volatile compound resembling RuO_4. Indeed, when in powder, osmium is very combustible, and even when compact it takes fire at a temperature scarcely exceeding the melting point of zinc, and its strong tendency to form this volatile oxide is the most striking character of the element. Its oxides and chlorides correspond almost precisely, both in composition and chemical relations, to those of ruthenium. The three lower oxides all form hydrates, but have no well-marked basic character. Osmic anhydride, OsO_3, is unknown, but potassic osmate, $K_2{=}O_2{=}OsO_2 . 2\,H_2O$, can easily be obtained in large rose-colored octahedrons. The volatile oxide, OsO_4, just referred to, forms colorless acicular crystals, which are very fusible, and freely soluble in water. It boils at about 100°, emitting an extremely irritating and deleterious vapor, whose pungent odor, resembling that of chlorine, is very characteristic. It is one of the most poisonous substances known, and

destroys germs which are scarcely affected by other poisonous agents. When pulverized osmium is heated in perfectly dry chlorine gas, there is first formed a blue-black sublimate of $OsCl_2$, and afterwards a red sublimate of $OsCl_4$. Osmious chloride gives a dark violet-blue solution, while osmic chloride gives a yellow solution; and when exposed to the air, the first rapidly changes to the last. By the action of reducing agents the change may be reversed. All the chlorides of osmium form double salts with the alkaline chlorides. The most interesting are the compounds corresponding to potassio-platinic chloride, $OsCl_4 . 2KCl$, which forms beautiful red octahedral crystals, sparingly soluble in water, and $[Os_2]Cl_6 . 6KCl . 6H_2O$, which resembles a characteristic Rhodium compound mentioned below.

387. **RHODIUM** ($Rh = 104.4$) is a very hard grayish white metal, barely fusible in an oxyhydrogen flame. *Sp. Gr.* after fusion 12.1. It is imperfectly malleable, but when alloyed with platinum may be easily worked. The pure metal is insoluble in acids, but, when alloyed in not too large quantity with platinum, copper, bismuth, or lead, it dissolves with them in aqua-regia. Although unalterable in the air, rhodium combines both with oxygen and chlorine at a red heat. It is readily oxidized by fusion with nitre or peroxide of barium. Fused with potassic bisulphate, it is converted into soluble rhodio-potassic sulphate, and when heated with sodic or baric chlorides in a current of chlorine gas, it yields various double salts, which are likewise easily soluble.

Although several oxides of rhodium have been distinguished, the only one which as yet has been well defined is Rh_2O_3, Rhodic Oxide, and this compound evidently marks the prevailing quantivalence of the element. In this condition, rhodium, unlike the elements with which it is associated, appears to be a well-marked basic radical, forming stable salts with several of the acids. Thus we have

Rhodic Hydrate,	$[Rh_2]^{vi}O_6^{ii}H_6$
Rhodic Acetate,	$[Rh_2]^{vi}O_6^{ii}(C_2H_3O)_6 . 5H_2O$
Rhodic Nitrate,	$[Rh_2]^{vi}O_6^{ii}(NO_3)_6 . 4H_2O$
Rhodic Sulphite,	$[Rh_2]^{vi}O_6^{ii}(SO)_3 . 6H_2O$
Rhodic Sulphate,	$[Rh_2]^{vi}O_6^{ii}(SO_2)_3 . 12H_2O$
Potassio-rhodic Sulphate,	$K_6.[Rh_2]^{xii}O_{12}^{xii}(SO_2)_6$

In like manner the only well-defined compound of rhodium and chlorine is $[Rh_2]^{vi}Cl_6$, a brownish red, indifferent body, insoluble in all

acids and alkalies. A solution of the chloride may be obtained by dissolving R_2O_3 in hydrochloric acid, and from this several well-crystallized soluble double chlorides may be prepared; as,

Potassio-rhodic Chloride,	$[Rh_2]Cl_6 \cdot 6\,KCl \cdot 6\,H_2O$
Sodio-rhodic Chloride,	$[Rh_2]Cl_6 \cdot 6\,NaCl \cdot 24\,H_2O$

They all have a ruby or rose color, whence the metal takes its name, from *ῥόδον, a rose.*

388. **IRIDIUM** (*Ir.* = 192.74) is a very hard white brittle metal. Though even less fusible than rhodium, it has been melted on lime with the oxyhydrogen flame and by the voltaic arc. *Sp. Gr.* after fusion 21.15. The pure metal is not acted on by any acid, but when alloyed with platinum it dissolves in aqua-regia. It may also be rendered soluble by fusion with alkaline reagents, under the same conditions as rhodium. Unless in very fine powder, it does not oxidize when heated in the air. It forms two principal oxides, Ir_2O_3 and IrO_2, and the corresponding hydrates are readily obtained. The hydrates dissolve in acids, but do not form definite oxygen salts unless associated with other basic radicals. There are also chlorides corresponding to the oxides, which form crystalline double salts with the alkaline chlorides, closely resembling the similar compounds already described. Thus we have

Potassio-iridious Chloride,	$[Ir_2]Cl_6 \cdot 6\,KCl \cdot 6\,H_2O$
Sodio-iridious Chloride,	$[Ir_2]Cl_6 \cdot 6\,NaCl \cdot 24\,H_2O$

which contain the radical $[Ir_2]^{\text{IV}}$, and also

Potassio-iridic Chloride,	$IrCl_4\,2\,KCl$
Sodio-iridic Chloride,	$IrCl_4 \cdot 2\,NaCl \cdot 6\,H_2O$

which contain the radical Ir^{IV}, the last class being less soluble than the first. Most of the compounds of iridium have a strong coloring power, those containing the radical $[Ir_2]^{\text{IV}}$ giving in general green, and those containing the radical Ir^{IV} red solutions. The iridic compounds are the most stable, but under the action of reducing or oxidizing agents one condition of the element readily passes into the other, and the changes of color which then take place, giving under different conditions beautiful shades of purple, violet, and blue, are very striking and characteristic. Hence the name Iridium, from *iris, the rainbow.* Under certain circumstances this element appears to manifest still other

degrees of quantivalence, and compounds containing both $Ir^{=}$ and $Ir^{\equiv}$ have been distinguished, the last acting as an acid radical in the product obtained by fusing iridium with nitre, which gives, with water, a deep blue solution, and is supposed to contain the compound $K_2{}^{=}O_2{}^{=}IrO_2$; but our knowledge on this subject is still very imperfect.

389. **PALLADIUM** ($Pd = 106.6$). *Sp. Gr.* = 11.4. — This brilliant white metal resembles platinum more closely than either of its associates. Although best known as a subordinate constituent of platinum ore, it has also been found (in Brazil) native, in masses of considerable size. It is harder than platinum, has less tenacity, and is not so ductile; nevertheless, it can be wrought with facility. It cannot be fused in an ordinary wind-furnace, but before the compound blowpipe it melts more readily than platinum, and if heated on lime is slowly volatilized, giving off a green vapor. Like the noble metals, its oxides and chlorides are reduced by heat alone. Yet when exposed to the air at a low red heat its surface becomes covered with an iridescent film of oxide, which is dispersed, however, at a higher temperature. Palladium is acted on by chemical agents more readily than platinum. Though only slightly attacked by pure hydrochloric or sulphuric acids, it dissolves readily in nitric acid, and also in aqua-regia, or in sulphuric acid when mixed with a small amount of nitric acid. It is also rendered soluble by fusion with alkaline reagents, under the same conditions as the preceding metals.

Palladium differs from the associated elements very markedly in that it affects most readily the condition of a bivalent positive radical. Thus we easily obtain, by dissolving the metal in the respective acids, the two following crystalline salts: —

Palladious Nitrate (Brown),	$Pd{=}O_2{=}(NO_2)_2$
Palladious Sulphate "	$Pd{=}O_2{=}SO_2 . 2\,H_2O$

The corresponding hydrate is precipitated by sodic carbonate from solutions of either of these salts, as a dark brown powder. The oxide, PdO, a black powder, is obtained by heating the nitrate to dull redness. The chloride, $PdCl_2$, forms brown hydrous crystals, when a solution of the metal in aqua-regia is evaporated to dryness, and by uniting with other chlorides yields definite crystalline salts, as, for example, $PdCl_2 . 2\,KCl$, which is easily obtained in dull yellow prismatic crystals.

Palladium also forms another class of compounds in which its atoms

are quadrivalent; but these are all very unstable. The chloride $PdCl_4$ has never been isolated, but the compound $PdCl_4 . 2KCl$, which has been obtained in red octahedral crystals, attests the relationship of this element to those with which it is classed.

But of all the characteristics of palladium the most noteworthy is the power which the metal possesses of absorbing hydrogen gas. It appears from the recent experiments of Professor Graham that, in the condition in which it is deposited by electrolysis, this metal will absorb or "occlude" nearly 1,000 times its volume of hydrogen, which amounts to about three fourths of one per cent of its weight, and in other conditions of the metal the power of absorption is very great, although not so large. The same phenomenon to a less degree has also been observed with platinum and iron, and considerable amounts of "occluded" hydrogen have been discovered in some of the meteors. The gas thus taken up by these metals is not simply mechanically condensed, as when absorbed by charcoal, but appears to be in a state of partial chemical combination, like that of a solution or an alloy; for we find that, while the hydrogen is easily expelled by heat, it shows no tendency to escape into a vacuum. The gas, however, readily passes through a heated palladium or platinum plate by an action similar to dialysis (§ 62), and these metals seem to partake more or less of a colloidal condition. By a similar action carbonic oxide passes through the iron walls of furnaces, and this class of phenomena, when further investigated, will undoubtedly be found to be quite general.

When a mass of palladium, charged as above described, is exposed to the air, it sometimes becomes suddenly heated from the oxidation of the hydrogen it contains, and the well-known power of platinum, especially when finely divided, as in the condition of *Sponge*, or the so-called *Platinum Black*, to determine the union of hydrogen and oxygen, and even to ignite a hydrogen jet, together with a large class of similar effects, may be explained on the same principle.

390. **Hydrogenium.** — The quantity of hydrogen "occluded" by palladium amounts to nearly one equivalent for each equivalent of the metal, and produces a marked change in its physical qualities. The volume of the metal is increased, its tenacity and conducting power for electricity diminished, and it acquires a slight susceptibility to magnetism, which the pure metal does not possess. From these facts Professor Graham inferred that the metal charged with gas is an alloy of palladium and metallic hydrogen, which he called *Hydrogenium*;

and it would appear that in this remarkable product the anticipations of chemists in regard to the metallic condition of hydrogen have been realized. If this inference is correct, and if, as is generally the case, the volume of the alloy is equal to the sum of the volumes of the two metals, then the *Sp. Gr.* of hydrogenium (deduced from that of the alloy) must be about 2. The chemical qualities of this alloy are very remarkable. It precipitates mercury from a solution of its chloride, and in general acts as a strong reducing agent. Exposed to the action of chlorine, bromine, or iodine, the hydrogen leaves the palladium and enters into direct union with these elements. Moreover, from a palladium wire charged with the gas, and covered with calcined magnesia (to render the flame luminous), the hydrogen burns, when lighted by a lamp, like oil from a wick. So far, therefore, as its chemical activities are concerned, hydrogenium bears somewhat the same relation to hydrogen gas that ozone bears to ordinary oxygen. Palladium plate or wire is most readily charged with hydrogen by making it the negative pole of a galvanic battery in the process of electrolyzing water. (Fig. 19.)

391. **PLATINUM.** $Pt = 194.8$. *Sp. Gr.* $= 21.5$. — The extended use of this metal in practical chemistry has made its appearance familiar to every student of the science. Platinum utensils have been of inestimable value in chemical investigations, on account of the infusibility of the metal, and its wonderful power of resisting chemical agents. It not only does not oxidize when heated in the air, but none of the acids singly act upon it, and even aqua-regia dissolves it but slowly. The metal is corroded when heated to redness in contact with the caustic alkalies or alkaline earths, especially the hydrates of lithium or barium, but the alkaline chlorides, carbonates, or sulphates may be fused in platinum crucibles without injuring them. Dry chlorine has no action on the metal at any temperature, and both the oxides and the chlorides are reduced by heat alone. Platinum, however, readily alloys with several of the other metals, and care must be taken to conduct no operations in platinum vessels by which a fusible metal may be reduced. Phosphorus and sulphur also act on platinum to a limited extent.

Platinum is very ductile and malleable, and two pieces of the metal may be welded together at a white heat, although to melt it the temperature of the oxyhydrogen flame is required. Melted platinum absorbs oxygen from the air, and, like silver (§ 161), spits if suddenly

cooled. The same phenomenon has been observed with palladium and rhodium.

392. **Chloroplatinates.** — When platinum is dissolved in aqua-regia, and the solution evaporated with hydrochloric acid until all the nitric acid is removed, brownish red prismatic crystals form, which are very deliquescent. These crystals have the composition $H_2PtCl_6 . 6H_2O$, and since the H_2 in the molecule are very readily replaced by basic radicals, the compound is now usually called chloroplatinic acid. From this acid a large number of salts are readily prepared, and these are the most important compounds of platinum. We have, for example, —

Chloroplatinic Acid,	$H_2PtCl_6 . 6H_2O$
Potassic Chloroplatinate,	K_2PtCl_6
Ammonic Chloroplatinate,	$(NH_4)_2PtCl_6$
Sodic Chloroplatinate,	$Na_2PtCl_6 . 6H_2O$
Magnesic Chloroplatinate,	$MgPtCl_6 . 6H_2O$
Baric Chloroplatinate,	$BaPtCl_6 . 4H_2O$

The chloroplatinates were formerly regarded as double salts, and the potassium salt, for example, was called potassio-platinic chloride, or the double chloride of platinum and potassium. The anhydrous platinic chloride has never been isolated.

These salts have all a characteristic yellow color except in the few cases where the second basic radical, having itself a strong coloring power, modifies the result. The barium and sodium salts crystallize in prisms. The magnesium salt, and the corresponding compounds of cadmium, zinc, copper, cobalt, and manganese, which are isomorphous with it, crystallize in rhombohedrons. The potassium and ammonium salts crystallize in regular octahedrons. The hydrous salts are all soluble in water, but the last two are nearly insoluble in water, and wholly insoluble in alcohol. They therefore can easily be obtained by precipitation, and on this fact are based several important methods of quantitative analysis. Moreover, compounds of the same general type may be formed with almost all the organic bases and vegetable alkaloids, and they furnish one of the simplest means of determining the molecular weight of such substances (§ 53).

393. **Chloroplatinites.** — If the solution of platinum in aqua-regia is evaporated over a water-bath, the brownish red residue dissolves either in water or in alcohol, and from the solution the compounds

described in the last section may be prepared. But if the residue of the evaporation is heated to 200°, chlorine escapes, and an insoluble greenish brown solid is obtained, which is essentially platinous chloride, $PtCl_2$. Platinous chloride thus prepared is not acted on even by nitric or sulphuric acids, but, out of contact with the air, it dissolves unchanged in hydrochloric acid. From this solution crystalline salts may be readily prepared, which have been called chloroplatinites. For example, —

Ammonic Chloroplatinite,	$(NH_4)_2PtCl_4$
Potassic Chloroplatinite,	K_2PtCl_4
Argentic Chloroplatinite,	Ag_2PtCl_4
Zincic Chloroplatinite,	$ZnPtCl_4$
Baric Chloroplatinite,	$BaPtCl_4$

These compounds may also be regarded as double salts.

394. **Platinous Hydrate**, $Pt{=}Ho_2$, which is obtained as a black powder by digesting platinous chloride with a solution of caustic potash, dissolves both in alkalies and acids, but the compounds thus formed are very unstable. Platinous nitrite and sulphite, however, form crystallizable double salts with several of the more basic radicals, which are best regarded as platino-nitrites and platino-sulphites respectively. Platinic hydrate, $Pt{=}Ho_4$, prepared indirectly from platinic chloride, is also soluble both in acids and alkalies. The compounds thus formed are all unstable, those in which the element acts as an acid radical being the more definite. Platinic sulphate and platinic nitrate, although they have not been crystallized, are easily obtained in solution, the sulphate by evaporating a solution of the chloride with sulphuric acid, the nitrate by decomposing the sulphate with baric nitrate. Lastly, by cautiously heating the hydrates, we can obtain the corresponding oxides; but if the temperature exceeds a certain degree, they are at once completely reduced.

By acting on different platinum salts with ammonia, a remarkable class of compounds have been obtained, which are best regarded as salts of platinum bases, and as formed by the coalescing of two or more molecules of H_3N soldered together by atoms of Pt or Pt_2, although they probably contain in some cases more complex platinum radicals. Similar compounds have also been formed with palladium and iridium; but, although highly interesting subjects of study on account of their manifold types and complex constitution, this new

class of ammonia bases illustrate no principles not already fully discussed, and for a description of them we must refer to more extended works.

QUESTIONS AND PROBLEMS.

1. Calculate the percentage composition of platinum ore, eliminating from the results given in § 384 the quantity of Iridosmine and sand with which the ore is mixed.

2. Explain the old method of working platinum ores, and illustrate the various steps in the process by reactions. To what extent are the associated metals precipitated by ammonic chloride?

3. Point out the relationship between the platinum metals and iron. Compare also these elements with each other, and consider especially the characteristics distinguishing the three groups into which they have been divided in Table II.

4. By what characters are the platinum metals as a class chiefly marked? Make a table which will bring into comparison the different double chlorides of these elements.

5. Explain, on the principle of dialysis, the transmission of hydrogen gas through the walls of a heated palladium or platinum tube.

6. Regarding the hydrogen condensed by platinum as chemically combined with the metal, can you find in this circumstance an explanation of the enhanced energy of the gas when in this condition? Consider the polarization of the negative platinum plate in a voltaic cell as an illustration of the same principle.

7. Write the symbols of the chloroplatinates and chloroplatinites on the assumption that they are double salts.

8. Show in what way the platinic salts may be used to determine the molecular weight of an organic base, and give an illustration of the principle.

9. Write the reactions by which platinic sulphate and nitrate may be prepared.

10. Write the reaction of a solution of platinic chloride on a solution of potassic nitrate. Platinic nitrate is one of the products.

11. Write the reaction of sodic carbonate on a solution of platinic sulphate, assuming that the chief product is platinic hydrate.

12. Write the reactions by which platinous hydrate may be prepared.

13. When platinous chloride dissolves in hydrochloric acid in contact with the air, what is the reaction?

14. Make a scheme illustrating the constitution or relations of the more important compounds of the platinum bases.

15. Explain a method of separating the platinum metals from each other.

DIVISION XXVII.

395. **TITANIUM.** $Ti = 50$. — Quadrivalent. No compounds corresponding to a lower degree of quantivalence are with certainty known. A comparatively rare element, but not unfrequently associated with iron. The most abundant native compound is Menaccanite, or Titaniferous Iron, whose symbol has already been given among the iron ores. This mineral, however, is in most cases an isomorphous mixture of $(Ti\text{-}Fe)O_3$ and Fe_2O_3, sometimes containing also magnesium and manganese, and thus arise the numerous varieties which have been distinguished. The other important compounds are, —

Rutile, Brookite, and Octahedrite (2d or 4th system),		TiO_2
Perofskite,	(Rhombohedral),	$Ca{=}O_2{=}TiO$
Sphene,	(Monoclinic),	$(Ca\text{-}O\text{-}Ti){\equiv}O_4{=}Si$

Titanium is also associated with columbium, tantalum, cerium, yttrium, and zirconium in a number of rare minerals.

396. **Metallic Titanium** has never been obtained as a massive metal, and its properties are very imperfectly known. As formed by decomposing the potassio-titanic fluoride with potassium it is a dark-green powder, showing under the microscope the color and lustre of iron. In this condition it is very combustible, readily dissolves in hydrochloric acid, and even decomposes water at the boiling point.

397. **Titanic Chloride,** $TiCl_4$, is obtained by passing chlorine gas through an intimate mixture of titanic oxide and carbon intensely heated. It is a heavy, colorless liquid, boiling at 135°, and yielding a vapor whose Sp. Gr. = 98.65. Exposed to the air it absorbs moisture, and gradually solidifies, forming a crystalline hydrate which readily dissolves in water. From this solution, if sufficiently dilute, almost the whole of the titanium is precipitated as a hydrate on boiling, and the same is true of the solution formed by dissolving the native oxides (after fusion with an alkaline carbonate) in hydrochloric acid.

398. **Titanous Chloride,** Ti_2Cl_6, is formed by passing a mixture of $TiCl_4$ and H-H through a red-hot porcelain tube. The compound is thus obtained in dark violet scales, which readily dissolve in water forming a violet solution; but in contact with the air this solution grad-

ually loses its color and deposits titanic hydrate. The same color is produced by boiling with tin a solution of titanic oxide in hydrochloric acid, and this reaction is the best test for titanium. The solution of titanous chloride is a very powerful reducing agent, which indicates that the radical $[Ti_2]^{\equiv}$ is not a stable condition of the element.

399. **Titanic Bromide and Iodide,** $TiBr_4$ and TiI_4, are fusible and volatile crystalline solids.

400. **Titanic Fluoride,** TiF_4, is a fuming, colorless liquid, obtained by distilling a mixture of fluor-spar and titanic oxide with sulphuric acid. This compound is resolved by water into soluble hydro-titanic fluoride and insoluble titanic oxyfluoride.

401. **Hydro-titanic Fluoride,** $TiF_4 \cdot 2HF$, is the acid of a large class of salts which are easily made from the solution produced as just stated. The ammonium and potassium salts, which are the most important, both crystallize in white anhydrous scales.

402. **Titanic Hydrates.** — A large number of these hydrates have been distinguished, and they affect two very different modifications. Those obtained by precipitation with ammonia readily dissolve in acids, and when heated are converted into the anhydride with vivid incandescence. Those obtained by boiling dilute solutions of the chloride or sulphate are insoluble in all acids except strong sulphuric. They give off water more readily than the others, and the dehydration is not attended by the same incandescence. The composition of these hydrates depends on the temperature at which they are dried, and they may be regarded as derived from the normal hydrate by the method repeatedly illustrated and expressed by the general equation

$$n\,TiHo_4 - m\,H_2O = (O_m Ti_n)Ho_{4n-2m}. \qquad [360]$$

The two modifications have been obtained in the same degrees of hydration, and, so far as known, they are isomeric. Moreover, by dialysis a pure aqueous solution of titanic hydrate has been procured, which gelatinizes when concentrated, and evidently contains the compound in a colloidal condition.

403. **Titanic Oxide,** TiO_2, is chiefly interesting from the fact that it affects three different modifications, which are represented in nature by the minerals Rutile, Brookite, and Octahedrite. These three isomeric bodies differ from each other in crystalline form, in density, and in hardness. Rutile, the most abundant, has the greatest hardness and density. Its crystals are tetragonal and isomorphous with those of

SnO_2. Brookite, which stands next in hardness and density, affects forms of the orthorhombic system, which are approximately isomorphous with those of MnO_2. Lastly, Octahedrite is softer and less dense than either of the others, and its crystals, although tetragonal, differ essentially from those of Rutile. (Problem 2, page 262.) The same differences have been observed in crystals obtained artificially by decomposing TiF_4 or $TiCl_4$ with steam, and it is found that the nature of the product depends on the temperature at which the reaction takes place, the hardest and most dense crystals being formed at the highest temperature.

In its densest condition titanic oxide has a red color, and is insoluble in all acids; but the white anhydride, obtained by igniting titanic hydrate, is converted into a sulphate when heated with strong sulphuric acid, and may then be dissolved in water. The native oxides, also, may be rendered soluble by fusion with alkaline carbonates or bisulphates. It melts before the compound blowpipe.

404. **Titanous Oxide,** Ti_2O_3, is obtained as a black powder when a stream of hydrogen is passed over ignited TiO_2. It dissolves in sulphuric acid, forming a violet solution, from which the alkalies precipitate a brown hydrate. A similar reduction takes place, and the same violet color is produced, when TiO_2 is dissolved in fused borax or microcosmic salt, and the bead heated before the blowpipe on charcoal in contact with a small globule of tin.

405. **Titanic Sulphide,** TiS_2, is formed in large brass-yellow lustrous scales when a mixture of H_2S and $TiCl_4$ is passed through a glass tube heated to incipient redness. It is decomposed by water, and cannot, therefore, be obtained by precipitation.

406. **Nitrides.** — Titanium has a marked affinity for nitrogen, and combines with it in several proportions. When dry ammonia gas is passed over $TiCl_4$, it is rapidly absorbed, with great elevation of temperature, and the resulting brown-red powder has the symbol $(H_{12}N_4Ti)\equiv Cl_4$. This compound, heated in a stream of ammonia gas, yields a copper-colored substance, which is the nitride Ti_3N_4, and this, when further heated in a current of hydrogen, is converted into a second nitride (Ti_2N_2?) having a golden-yellow color and metallic lustre. A third violet-colored nitride has the symbol TiN_2. Lastly, the very hard copper-colored cubic crystals sometimes found adhering to the slags of iron-furnaces, and formerly mistaken for metallic titanium, have the composition expressed by the symbol Ti_3CN_4.

407. **TIN.** $Sn = 118.$ — Bivalent and quadrivalent. The last is the most stable condition. The only valuable ore of tin is the oxide SnO_2, called in mineralogy Cassiterite or Tin Stone, and this is found at but few localities, chiefly in Cornwall, Malacca, Bolivia, Australia, Bohemia, and Saxony. This element is also an essential constituent of Tin Pyrites $[Zn,Fe].[Cu_2].S_4.Sn$, and is associated with columbium, titanium, zirconium, etc. in a few rare minerals, but its range in nature, so far as known, is very limited.

The metal is obtained by reducing the native oxide with coal; but although in theory so simple, this process is in practice quite complicated. The ore requires, previous to smelting, a prolonged mechanical treatment, and in the furnace a large amount of metal passes into the slags, which therefore have to be worked over.

408. **Metallic Tin** has a familiar white color and bright lustre. It has a crystalline structure, and the breaking of the crystals against each other, when a bar of the metal is bent, produces the peculiar sound known as the *cry of tin*. By slowly cooling the fused metal distinct crystals can be obtained, which belong to the tetragonal system. The tenacity of tin is feeble, but it can readily be rolled and beaten into thin leaves, which are well known under the name of Tin foil. *Sp. Gr.* = 7.3. Melts at 222°. Boils at a white heat. Inferior conductor of heat or electricity.

Tin does not tarnish in a moist atmosphere which is free from sulphur, but when melted in the air it slowly oxidizes, and at a red heat decomposes steam. Hydrochloric acid dissolves the metal rapidly, the products being stannous chloride and hydrogen gas. It also dissolves slowly when boiled with dilute sulphuric acid, yielding stannous sulphate and liberating hydrogen as before. When the sulphuric acid is concentrated, SO_2 is evolved and stannous sulphate formed only so long as the tin is in excess. If the acid is in excess, sulphur separates, and the product is stannic sulphate. Very strong nitric acid does not act on the metal, but when somewhat diluted it converts the tin into a white hydrate, insoluble in an excess of the acid. Aqua-regia, if not too concentrated, dissolves tin as stannic chloride, and the alkaline hydrates and nitrates also act upon it at a high temperature.

Tin unites directly with most of the non-metallic elements, and forms alloys with many of the metals. The alloys with copper have already been mentioned. Pewter and plumber's solder are alloys of tin and lead; Britannia metal is an alloy of brass, tin, lead, and bis-

muth; and the silvering of mirrors, an amalgam of tin and mercury. On account of its beautiful lustre and power of resisting atmospheric agents, tin is much used for coating other metals. The common tin-ware is made of sheet-iron thus protected.

409. **Stannous Chloride.** $SnCl_2$. — The anhydrous compound (Butter of Tin) obtained by heating mercuric chloride with an excess of tin, or by heating the metal in hydrochloric acid gas, is a fusible white solid with a fatty lustre, soluble in water and alcohol. The hydrous salt (tin salts), formed by crystallizing the solution of tin in hydrochloric acid, has the symbol $SnCl_2 . 2\,H_2O$. The pure crystals dissolve perfectly in a small amount of water, free from air, but a large amount of water produces a partial decomposition.

$$(2\,SnCl_2 + 3\,H_2O + Aq) = \mathbf{Sn_2OCl_2 . 2\,H_2O} + (2\,HCl + Aq). \quad [361]$$

So, also, when the solution is exposed to the air.

$$(6\,SnCl_2 + 4\,H_2O + Aq) + \text{O-O} = 2(\mathbf{Sn_2OCl_2 . 2\,H_2O}) + (2\,SnCl_4 + Aq). \quad [362]$$

The oxychloride, which is milk-white and insoluble (even in dilute acids), renders the solution in both cases turbid. Free hydrochloric acid, tartaric acid, and sal ammoniac prevent the decomposition. Owing to the unsatisfied affinities of the tin radical, stannous chloride is a powerful reducing agent (§ 260), and is much used for this purpose both in the laboratory and the dye-house. It also acts as a mordant. Lastly, it forms salts with several of the metallic chlorides.

Potassio-stannous Chloride,	$SnCl_2 . 2\,KCl . (1, 2, \text{or } 3)\,H_2O$
Bario-stannous Chloride,	$SnCl_2 . BaCl_2 . 4\,H_2O$

410. **Stannic Chloride,** $SnCl_4$, may be made either by distilling a mixture of tin and mercuric chloride, the last being in excess, or by heating tin in chlorine gas. It is a colorless, fuming liquid, boiling at 115°, and yielding a vapor whose Sp. Gr. = 132.7. The liquid, exposed to the air, eagerly absorbs moisture, and changes into a crystalline solid. When mixed with water, intense heat is evolved, and a solution formed which yields on evaporation rhombohedral crystals of $SnCl_4 . 5\,H_2O$. These crystals, dried *in vacuo*, lose $3\,H_2O$, and there is reason to believe that the remaining $2\,H_2O$ are a part of the molecule of the salt. If we regard the atoms of chlorine as trivalent, we can easily see that such an atomic group would be possible, for we

might then have the univalent radical $(H\text{-}Cl\text{=}Cl) = Hcl$ replacing H_2, and the symbol of the dried salt would be written $Sn\equiv Ho_2, Hcl_2$. The same principle may be applied in other cases where the violence of the action indicates that a chemical union has taken place between an anhydrous chloride and water. Such bodies, however, may also be regarded as chlorhydrines (§ 280), to which molecules of HCl are united in place of water of crystallization. Thus the symbol of the hydrous chloride we have been discussing might be written $Sn\equiv Cl_2, Ho_2 \,.\, 2\,HCl$.

Although stannic chloride forms a clear solution with a small amount of water, copious dilution determines the precipitation of the greater part of the tin as an insoluble stannic hydrate. Heat favors this decomposition, and, on the other hand, the presence of a large excess of hydrochloric acid prevents it. Stannic chloride unites with a considerable number of bodies both organic and inorganic, and forms double salts with several of the metallic chlorides. Ammonio-stannic chloride, $SnCl_4 \,.\, 2\,NH_4Cl$ (Pink Salts of the dyers), is isomorphous with the corresponding compound of platinum. An impure solution of $Sn\,Cl_4$, made by dissolving tin in aqua-regia, is also extensively used in dyeing for brightening and fixing certain red colors.

There are two bromides and iodides of tin corresponding to the chlorides. There is also a stannous fluoride, and, although stannic fluoride has not been isolated, a large number of double stannic fluorides or fluostannates are known, which are isomorphous with the corresponding compounds of titanium and silicon.

411. **Hydrates. — Stannous Hydrate,** the precipitate which falls on adding an alkaline carbonate to a solution of stannous chloride, is said to have the composition $Ho_2\text{=}(Sn_2\text{=}O)$. It is soluble in both alkalies and acids. Boiled with water or a weak solution of potash it is rendered anhydrous; but if boiled with a concentrated solution of this alkali, it yields potassic stannate and metallic tin. The moist hydrate absorbs oxygen from the air, and acts, like the chloride, as a reducing agent. The only important oxygen salt corresponding to this hydrate is stannous sulphate.

Stannic Hydrate, like titanic hydrate, affects both a soluble and an insoluble modification. The hydrate precipitated when ammonia is added to a solution of stannic chloride dissolves readily both in acids and alkalies, while that obtained by boiling the same solution greatly diluted, or by acting on tin with nitric acid, is insoluble in

acids, and dissolves less readily than the first in alkalies. The composition of these bodies varies with the temperature at which they are dried, and they are usually distinguished as stannic and metastannic hydrates. Like the corresponding compounds of titanium, they may be regarded as derived from a normal hydrate of either class by the elimination of successive molecules of water. The salts obtained by dissolving stannic hydrate in oxygen acids are unimportant. The sulphate is the most stable, but this is completely decomposed, and the tin precipitated as metastannic hydrate, when the aqueous solution is diluted and boiled. The compounds in which the atom $Sn^{\equiv}$ acts as an acid radical are much more stable. The alkaline stannates crystallize readily, and both potassic and sodic stannates, $(K \text{ or } Na)_2^{=}O_2^{=}SnO \,.\, 4\,H_2O$, are commercial products much used as mordants. Their efficacy depends on the fact that ammonic chloride and all acids, even the CO_2 of the atmosphere, decompose these salts when in solution, and the stannic hydrate thus precipitated in the fibre of the cloth binds the coloring matter.

The compounds obtained by dissolving metastannic hydrate in alkaline solvents cannot be crystallized, but are precipitated on adding to the solution caustic potash. The potassium salt thus obtained, dried at 126°, has the composition $K_2^{=}O_2^{=}Sn_5O_9 \,.\, 4\,H_2O$. It was formerly supposed that the peculiar qualities of the metastannic hydrates and the metastannates were due to the atomic grouping here represented, but this opinion has not been sustained by recent investigations. The water represented as water of crystallization cannot be removed without decomposing the salt, and is evidently water of constitution; so that we have good reason for writing the symbol $H_8,K_2^{x}O_{10}^{x}(Sn_5O_5)$, after the type of the normal stannates, and we may regard it as an example of the soluble colloidal hydrates, to which we have before referred (§ 268). This view harmonizes with the facts, that, on boiling an aqueous solution of this compound, metastannic hydrate is precipitated, and that by dialysis a solution of both metastannic and stannic hydrates in pure water may be obtained. The two classes of compounds are probably isomeric, but differ in the degree of molecular condensation.

412. **Oxides.** — Stannous oxide, SnO, may be obtained in various ways, and its color differs according to the mode of preparation. It has a strong affinity for oxygen, and, if set on fire when dry, burns to stannic oxide.

Stannic oxide has been crystallized artificially, not only in the forms of Tin Stone isomorphous with Rutile, but also in forms isomorphous with Brookite. As obtained by igniting the hydrate, or by burning metallic tin, it is an amorphous white powder. It offers even greater resistance to the action of chemical agents than TiO_2. It is not attacked by acids, even when concentrated. It is not dissolved by fusion with alkaline carbonates, but is rendered soluble by fusion with caustic alkalies. It is also taken up when fused with acid potassic sulphate, but separates completely when the fused mass is dissolved in water. Moreover, like titanic oxide, it is very hard and infusible, but, unlike that, it is reduced to the metallic state when ignited in a stream of hydrogen gas.

Besides SnO and SnO_2 an intermediate oxide, Sn_2O_3, has been distinguished, but it does not form definite salts. Dissolved in hydrochloric acid it gives with auric chloride the beautiful purple precipitate known as Purple of Cassius (§ 295).

413. **Sulphides.** — The dark-brown precipitate which falls when H_2S is passed through an acid solution of a stannous salt is SnS, and the dull yellow precipitate which forms under the same circumstances in a solution of a stannic salt is a hydrate of SnS_2. The last of these dissolves readily in solutions of alkaline sulphides, and forms with them definite salts. It is also soluble in the fixed alkaline hydrates, and in either case is precipitated unchanged when the alkali is neutralized with an acid. *Stannous* sulphide, on the other hand, does not form salts with the alkaline sulphides, and does not dissolve in solutions of these compounds, unless, like the common yellow ammonic sulphide, they contain an excess of sulphur, when it is converted into SnS_2, and as such is precipitated on neutralizing the alkali. It does, however, dissolve in the fixed alkaline hydrates; but when an excess of acid is added to the solution, a yellow precipitate of SnS_2 falls, containing only one half of the tin present.

The beautiful yellow flaky material known as mosaic gold, and used in painting to imitate bronze, consists of anhydrous stannic sulphide, and is obtained by subliming a mixture of tin, sulphur, sal ammoniac, and mercury. There is also a sesquisulphide, Sn_2S_3.

414. **Compounds with the Alcohol Radicals.** — These compounds are very numerous and highly important theoretically, because they establish beyond all doubt the atomic relations of tin. Compounds have been obtained containing methyl, ethyl, and amyl, either singly

or associated together. Three compounds are known containing only tin and ethyl. Putting $(C_2H_5) = Et$, we have

$$Sn{=}Et_2, \qquad (Sn{=}Et_3){-}(Sn{\equiv}Et_3), \qquad Sn{\equiv}Et_4.$$

All three are colorless oily liquids. The last is the most stable, boiling at 181°, and yielding a vapor whose Sp. Gr. = 116. The others cannot be volatilized without decomposition, and unite directly with oxygen, chlorine, bromine, and iodine. The first, especially, like other stannous compounds, acts as a reducing agent, absorbing oxygen from the air, and precipitating silver from a solution of the nitrate. This is the only stannous compound known among this class of bodies. In all the others the tin atoms exert their maximum atom-fixing power, and they may be regarded either as compounds of the radicals $(SnEt_2)''$ or $(SnEt_3)'$, or else as formed from stannic ethide by replacing either one or more of the atoms of ethyl by other radicals. The following are a few examples: —

Stanno-diethylic Bromide,	$(SnEt_2)''Br_2$
Stanno-diethylic Oxide,	$(SnEt_2)''O$
Stanno-diethylic Acetate,	$(SnEt_2)''O_2''(C_2H_3O)_2$
Stanno-diethylic Sulphate,	$(SnEt_2)''O_2''SO_2$
Stanno-triethylic Chloride,	$(SnEt_3)'Cl$
Stanno-triethylic Hydrate,	$(SnEt_3)'O'H$
Stanno-triethylic Oxide,	$(SnEt_3)_2''O$
Stanno-triethylic Carbonate,	$(SnEt_3)_2''O_2''CO$

The methyl and amyl compounds are formed after the same analogy, and also others which contain both methyl and ethyl. These compounds are either liquids or crystalline solids. The chlorides, bromides, and iodides are, as a rule, volatile, and sparingly soluble in water. The oxides and oxygen salts, on the other hand, generally dissolve freely in water, and are more easily decomposed by heat. The vapor densities of several of these compounds are given in Table III., and this list might be greatly extended.

DIVISION XXVIII.

415. **ZIRCONIUM.** $Zr = 89.6$. — Quadrivalent. Found only in Zircon, Eudialyte, and a few other very rare minerals. The elementary substance closely resembles silicon. It may be obtained by similar reactions in three corresponding states, amorphous, crystalline and graphitoidal. Amorphous zirconium is a very combustible black powder. The crystals, *Sp. Gr.* 4.15, resemble antimony in color, lustre, and brittleness, and burn only at a very high temperature. The graphitoidal variety forms very light steel-gray scales. Zirconium is very infusible, is but slightly attacked by the ordinary acids, but by hydrofluoric acid, and in some conditions aqua-regia, dissolves rapidly.

416. **Zirconic Chloride,** $ZrCl_4$, is a white volatile solid (Sp. Gr. = 117.6), which dissolves easily, and with evolution of heat, in water. This solution, or the solution of the hydrate in hydrochloric acid, yields on evaporation a large mass of white silky needles, which, when heated, lose water and hydrochloric acid, leaving an oxychloride $Zr_2O_3Cl_4$.

417. **Zirconic Fluoride,** ZrF_4, is likewise a volatile white solid, and forms a crystalline hydrate, $ZrF_4 . 3H_2O$, which is decomposed by heat, leaving pure ZrO_2. Zirconic fluoride unites with many other metallic fluorides, forming salts which are isomorphous with the corresponding compounds of silicon, titanium, and tin. The following symbols illustrate the known types :—

Cadmio-zirconic Fluoride,	$ZrF_4 . 2CdF_2 . 6H_2O$
Tripotassio-zirconic Fluoride,	$ZrF_4 . 3KF$
Dipotassio-zirconic Fluoride,	$ZrF_4 . 2KF$
Potassio-zirconic Fluoride,	$ZrF_4 . KF . H_2O$
Sodio-zirconic Fluoride,	$2ZrF_4 . 5NaF$

418. **Zirconic Hydrate,** precipitated from the chloride by ammonia, and dried at 17°, has the symbol $Zr_2H_8O_4$. Dried at a higher temperature, $(ZrO)_2H_2O_2$. It is a yellowish, translucent, gummy mass, having a conchoidal fracture. The hydrate precipitated and washed cold dissolves easily in acids, and to a slight extent even in water; but when precipitated from hot solutions, or washed with hot water,

it dissolves only in concentrated acids. Zirconic hydrate acts both as a base and an acid.

There are several zirconic sulphates. The normal salt can be crystallized, and the formation of a basic sulphate, which is precipitated when a neutral solution of zirconia in sulphuric acid is boiled with potassic sulphate, is one of the most characteristic reactions of zirconium. The salts of zirconium have an astringent taste, and the solutions redden turmeric paper.

The precipitated hydrate is insoluble in caustic alkalies; but when precipitated by a fixed alkaline carbonate, or, better, by a bicarbonate, it dissolves in an excess of the reagent. The alkaline zirconates can be obtained by fusion, and several definite crystalline zirconates of the more basic radicals have been studied.

419. **Zirconic Oxide (Zirconia)**, ZrO_2, is obtained by heating the hydrate. Prepared at the lowest possible temperature, it forms a white, tasteless powder, soluble in acids; but when heated to incipient redness it glows brightly, becomes denser and much harder, and is then insoluble in any acid excepting hydrofluoric or strong sulphuric acid. Zirconia has been crystallized artificially in the same form as Tin Stone and Rutile.

The mineral Zircon is usually regarded as a silicate of zirconium, $Zr\equiv O_4\equiv Si$, but the symbol may also be written $[Zr,Si]\equiv O_2$, and this view harmonizes with the fact that the crystalline form is almost identical with that of ZrO_2, SnO_2, and TiO_2. Moreover, several isomorphous varieties of this mineral are known (Malacone, Oerstedite, etc.) in which the proportions of Zr and Si are quite variable. They are more or less hydrous, and for the most part comparatively soft; but, like pure ZrO_2, they become, when heated, exceedingly hard, as well as more dense.

420. **THORIUM.** $Th = 115.7$. — The mineral Thorite, or Orangeite, is essentially a hydrous silicate of this exceedingly rare metallic element, which has also been found, but only as a subordinate constituent, in Euxenite, Pyrochlore, Monazite, Gadolinite, and Orthite. When Thorite is decomposed by hydrochloric acid, a solution of thoric chloride, $ThCl_4$, is obtained, from which the caustic alkalies precipitate a hydrate insoluble in an excess of the reagent. A similar precipitate is obtained with the alkaline carbonates, but this readily dissolves when an excess is added to the solution. In the same solution a precipitate is obtained with oxalic acid, potassic sulphate, and potassic ferrocyanide.

As the above reactions indicate, Thorium is allied in many of its properties to the metals of the glucinum and cerium groups; but in other respects it resembles more nearly zirconium, with which it is here associated. The anhydrous oxide ThO_2 is a white powder, which glows when heated, becomes more dense, and after ignition is insoluble in any acid except concentrated sulphuric. It has a high specific gravity, and by fusion with borax has been obtained in tetragonal crystals (Fig. 57) resembling those of Tin Stone, SnO_2, and Rutile, TiO_2. The anhydrous chloride is volatile, and the hydrated chloride forms a radiate crystalline mass, like $ZrCl_4$. The chloride may be reduced by sodium, and the metal may be thus obtained as a gray lustrous powder, which readily burns in the air.

QUESTIONS AND PROBLEMS. (Divisions XXVII., XXVIII.)

Titanium.

1. Compare by means of graphic symbols the composition of Perofskite and Menaccanite. Can they be regarded as similarly constituted?

2. Write the reaction by which titanic chloride is made.

3. According to the experiments of Isidore Pierre, 0.8215 gramme of $TiCl_4$ yields 2.45176 grammes of $AgCl$. Calculate the atomic weight of titanium, and state clearly the course of reasoning by which the result is reached. Ans. 50.34.

4. Write the reaction which takes place when a dilute aqueous solution of $TiCl_4$ is boiled.

5. Write the reactions which take place when a solution of titaniferous iron in hydrochloric acid is boiled with tin, and explain the use of this reaction as a test for titanium.

6. Write the reaction by which TiF_4 is prepared, and also show how it is decomposed by water.

7. Represent the constitution of hydro-titanic fluoride by a graphic symbol, assuming that F is trivalent.

8. Represent in a tabular form the possible titanic hydrates.

9. Do the hydrates of any of the preceding elements present phenomena similar to those of titanic hydrate?

10. Write the reaction by which TiS_2 is prepared, and also the reactions by which crystals of TiO_2 may be obtained.

ic gravities and hardness of the native titanic
differences indicate in regard to the molecular
rals?

phic symbols the constitution of the nitrides of

logies between titanium and the platinum metals.
related to iron?

Tin.

tions of hydrochloric, nitric, and sulphuric acid on

tion of stannous chloride on solution of $HgCl_2$.

action by which anhydrous $SnCl_2$ is prepared.

tions [361] and [362], and explain the use of tin salts as

eactions by which anhydrous $SnCl_4$ is prepared.

the constitution of hydrous stannic chloride by graphic
ly the same principle to the interpretation of other similar

e reaction when a dilute aqueous solution of stannic chloride
explain the use of this solution as a mordant.

the reaction which takes place when stannous hydrate is boiled
ntrated solution of potassic hydrate.

a table exhibiting the possible stannic hydrates, and explain
ce between the two classes of these compounds.

te the reaction which takes place when a dilute aqueous solution
sulphate is boiled.

ite the reaction which takes places when a solution of sodic stan-
oiled with ammonic chloride.

epresent the constitution of metastannic hydrate by graphic sym-
d explain the two opinions which have been entertained in regard
owing how far they are sustained by facts.

Vrite the reaction of H_2S on a solution of stannous or stannic chloride.

Vrite the reaction which takes place when SnS is dissolved in yellow
le sulphide, and that which follows on neutralizing the alkaline
with an acid. Write also the reactions when an alkaline hydrate is
solvent.

28. Point out the analogies and the differences between tin and titanium. By what simple reaction may the two elements be separated when in solution?

29. How is tin related to the platinum metals?

30. According to the experiments of Dumas, 100 parts of tin, when oxidized by nitric acid, yield 127.105 parts of SnO_2. What is the atomic weight of the element, assuming that the oxide has the constitution represented by the symbol? Ans. 118.06.

31. On what facts do the conclusions in regard to the atomicity of tin and the constitution of its several compounds rest?

32. Show that the atomic weight of tin, deduced from the percentage composition and vapor densities of its compounds with the alcohol radicals, agrees with the value given above. Show, also, that these compounds fully illustrate the atomic relations of the elements.

33. State the reasons for classing zirconium and thorium with tin and titanium.

34. Point out the resemblances between zirconium and silicon, and give the reasons for classing Zircon with Tin Stone and Rutile.

35. The compounds formed by the fluorides, chlorides, bromides, etc. of the elements of the last three sections have been usually represented as double salts. May they not, however, be regarded as constituted after the type of the chloroplatinates and chloroplatinites (§§ 392 and 393?) Consider whether there is any real ground for a distinction between the compounds of this same general class. Consider also in this connection the suggestion in § 410.

DIVISION XXIX.

421. **SILICON.** $Si = 28$. — Quadrivalent. Most abundant of the elements after oxygen, forming, as is estimated, about one fourth of the rocky crust of the globe. Always found in nature united with oxygen, either as Quartz, SiO_2, or associated with more basic radicals in the various native silicates, many of whose symbols have already been given (§§ 264, 283). The elementary substance may be obtained in three different conditions, — amorphous, graphitoidal, and crystalline.

1st. By decomposing $SiF_4 . 2KF$ with potassium or sodium, or by heating the same metals in a current of the vapor of $SiCl_4$, silicon is obtained as a dull-brown powder, which soils the fingers, and readily dissolves in hydrofluoric acid or a warm solution of caustic potash, although insoluble in water and the common acids. When ignited it burns brilliantly, but the grains soon become coated with a varnish of melted silicon, which protects them from the further action of the air.

2d. The brown powder just described, when intensely heated in a closed crucible, becomes very much denser and darker in color, and afterwards is insoluble in hydrofluoric acid, and does not burn even in the oxyhydrogen flame. It does dissolve, however, in a mixture of hydrofluoric and nitric acids, or in fused potassic carbonate, and it deflagrates if intensely heated with nitre.

3d. At the highest temperature of a wind-furnace silicon melts, and may be cast into bars which have a crystalline structure, a submetallic lustre, and a dark steel-gray color. Moreover, by reducing silicon in contact with melted aluminum or zinc, the molten metal dissolves the silicon, and afterwards, on cooling, deposits it in definite crystals. These crystals have a reddish lustre and the form of diamond, which they almost rival in hardness.

422. **Silicic Anhydride or Silica.** SiO_2. — By far the most abundant of all mineral substances. The mineralogists distinguish two principal modifications, Quartz and Opal. Quartz crystallizes in the hexagonal system (Figs. 84 to 87), has a *Sp. Gr.* of 2.5 to 2.8, is so hard that it cannot be cut with a file, and even in powder is but slightly acted on by hot solutions of caustic alkalies. Opal is amorphous or colloidal, has a *Sp. Gr.* of 1.9 to 2.3, is easily abraded with a

file, and dissolves in alkaline solutions. Each of these mineral species exhibits numerous varieties, determined by differences of structure or admixtures of different bodies. Among those of Quartz may be mentioned Common Quartz, Milky Quartz, Smoky Quartz, Amethyst, Chalcedony, Carnelian, Agate, Onyx, Flint, Hornstone, Jasper, Sandstone, and Sand. Among those of Opal we have Precious Opal, Common Opal, Jasper Opal, Wood Opal, Siliceous Sinter, Float Stone, and Tripoli. These two conditions of SiO_2, however, are sometimes found alternating on the same specimen, and the chalcedonic varieties of Quartz have frequently the appearance of Opal, through which state they probably passed in the process of formation. The Opals are more or less hydrous, but the water present is usually regarded as unessential.

Both in its crystalline and in its amorphous condition silica is insoluble in water, and in all acids excepting hydrofluoric acid, which is its appropriate solvent. The heat of the oxyhydrogen flame is required for its fusion, but at this temperature it melts to a transparent glass, and may be drawn out into fine flexible elastic threads, the fused silica affecting the amorphous condition. When added in powder to melted sodic or potassic carbonate it causes violent effervescence, and if the silica is pure the product is a colorless glass. Unless the silica is in great excess, the alkaline silicates thus obtained are soluble in water, and are generally known as *soluble* or *water glass*. They yield alkaline solutions, which are very much used in the arts, — 1. As a cement for hardening and preserving stone; 2. In preparing walls for fresco-painting; 3. For mixing with soap; and 4. In preparing mordanted calico for dyeing. The same solutions can be also made by digesting flints in strong solutions of the caustic alkalies at a high temperature under pressure.

423. **Silicic Hydrates.** — If to a solution of an alkaline silicate in water hydrochloric acid be added gradually, a gelatinous precipitate of silicic hydrate is formed, which, in its initial condition, probably has the composition Ho_4Si; but in drying it passes through every degree of hydration, and the various hydrates which have been obtained in this and in other ways may be represented by the general formula

$$nHo_4Si - mH_2O = Ho_{4n-2m}(O_nSi_n). \qquad [365]$$

They are all, however, very unstable bodies, some losing water at low temperatures, and others very hygroscopic, so that it is difficult to obtain definite compounds.

If, instead of making the experiment as just directed, a dilute solution of an alkaline silicate be poured into a considerable excess of hydrochloric acid, no precipitate is formed. The whole of the hydrate remains in solution mixed with the alkaline chlorides and free hydrochloric acid. These crystalloid substances, however, can readily be separated by dialysis from the colloid hydrate, and a pure solution of silicic hydrate may be thus obtained, containing as much as five per cent of SiO_2. Moreover, by boiling in a flask, the solution may be concentrated, until the quantity of silica reaches fourteen per cent. This solution is limpid, colorless, tasteless, and has a feebly acid reaction, which a very small quantity of *K-Ho* is sufficient to neutralize.

Evidently, then, silicic hydrate has both a soluble and an insoluble modification, but the last is by far the most stable condition. The concentrated solution, formed as above, in a few days completely gelatinizes. Moreover, even in a closed vessel this jelly gradually shrinks, spontaneously squeezing out the greater part of the water, until at last it becomes a hard mass, resembling Opal. When, however, the solution is quite dilute, it can be kept indefinitely without gelatinizing, and most spring and river waters hold an appreciable amount of silicic hydrate thus dissolved. The power of dissolving silica, which natural waters possess, is greatly enhanced by the presence of alkaline carbonates; and when the action of the alkaline liquid is aided by a high temperature, as in the case of hot springs, large quantities of silica are frequently dissolved, and such solutions have undoubtedly exerted an important agency in the geological history of the earth. Whenever a solution of silicic hydrate is evaporated to dryness, the whole of the silica is rendered insoluble, and cannot afterwards be dissolved either in water or common acids.

424. **Silicates.** — Although it is impossible to isolate the numberless intermediate silicic hydrates comprehended in [363], yet we find in nature numerous mineral silicates formed after the same types, and which may be regarded as derived from the hydrates by replacing the hydrogen atoms with various basic radicals. These silicates, like silica itself, affect both the crystalline and the colloidal condition.

The crystalline silicates are represented by numerous well-defined mineral species, and by the rocks which are simply aggregates of such minerals. They have been formed in many ways; for example, — 1. By deposition from solution; 2. By the action of heated water or vapor on igneous and sedimentary rocks; 3. By the slow cooling of molten siliceous material.

The colloidal silicates are represented by the Obsidians, the Pitchstones, and other volcanic rocks, which have probably always been formed by the sudden cooling of melted lavas. To the last class belong also the various artificial silicates we call Glass, and the Slags obtained in many metallurgical processes. Thus Crown Glass is a silicate of sodium or potassium with calcium; Flint Glass, a silicate of either of these alkaline radicals with lead; and the Slags are silicates of calcium, magnesium, aluminum, and iron, in various combinations. Since many of the basic hydrates and anhydrides may be melted with silica in almost every proportion, we do not find in the colloidal silicates the same definite composition as in the crystalline minerals, but they are probably in all cases mixtures of definite compounds.

Most of the silicates are fusible, and their fusibility is increased by mixture with each other. As a rule, those which contain the most fusible oxides melt the most readily, and the more readily in proportion as the base is in excess. Only the alkaline silicates above referred to are soluble in water. Most of the hydrous silicates, and many which are anhydrous, but contain an excess of base, are decomposed by acids;* but the anhydrous, normal, or acid silicates are, as a rule, unaffected by any acid except hydrofluoric, although they can be rendered soluble by fusion with an alkaline carbonate. When the fused mass is treated with $HCl + Aq$, evaporated to dryness, and again digested with the same acid, the silica remains as a gritty insoluble powder, and can at once be recognized. The presence of silica in a mineral can generally also be discovered by fusing a small fragment before the blowpipe with microcosmic salt. This decomposes the mineral, but does not dissolve the silica, which is left floating in the clear bead.

425. **Constitution of Native Silicates.** — The symbols of many of the native silicates have already been given, and those of others will be discovered by solving the problems which follow this division. Moreover, the principles on which these symbols are written have been fully developed. There is still, however, an uncertainty in regard

* Soluble compounds of the basic radicals are thus formed, while the silica separates, either as a gelatinous hydrate, or as a loose, anhydrous powder. Sometimes, however, the silica also dissolves, and generally it is taken up to a limited extent. In every case the silica becomes anhydrous and completely insoluble, if the solution is evaporated to dryness at the boiling point of water, and the residue heated a few degrees higher.

to the constitution of some of these minerals, and it is not always possible to deduce from the results of analysis a probable rational formula, even when these results are known to be essentially accurate. This uncertainty arises from several causes: — 1. We have no sure criterion of the purity of the mineral, since we are not able, as in the case of artificial products, to eliminate admixtures by repeated crystallizations. 2. The methods commonly used to determine the molecular weight of compounds (§ 53) entirely fail in the case of these silicates, and this important element for fixing the symbol is therefore wanting* (§ 24). Moreover, when the molecule is condensed, (that is, contains several atoms of silicon,) unavoidable inaccuracies in the processes may vitiate conclusions based on analysis alone. 3. The constant replacement of one radical by another (§ 365) renders the composition of most silicates very complex, and we are frequently at a loss to determine the part which a given radical may play in the compound. This is especially true of hydrogen, for we have no certain means of deciding whether the atoms of this element in a hydrous silicate are a part of the molecule itself, or only connected with it in the water of crystallization.

426. **Symbols of Native Silicates.** — The composition of most native silicates may be so varied by replacements, without any essential change in external qualities, that such a mineral species cannot be distinguished as a compound of definite radicals, but merely as conforming to a certain general formula, and the only specific character is the ratio between the total quantivalence of the several composite radicals of which the mineral may be supposed to consist. This ratio we call the *atomic ratio.* Thus the composition of common Garnet may in general be represented by the formula

$$\overset{II}{R}_3, [\overset{VI}{R}_2]^{xii} O_{12}{}^{xii} \overset{IV}{Si}_3 ;$$

but $\overset{II}{R}$ may be either *Ca, Mg, Fe, Mn,* or *Cr,* and $[\overset{VI}{R}_2]$ either $[Al_2]$, $[Fe_2]$, or $[Cr_2]$, and Garnets have been analyzed in which these several radicals are mixed together in every conceivable way consistent with the general formula to which they all conform. *This formula, however, is merely the expression of a definite ratio between the quantivalence or*

* We have reason to hope that a more accurate knowledge of the laws which govern the molecular volume of compounds in the solid condition may hereafter supply this deficiency.

atomicities of the several classes of radicals taken as a whole, and in the last analysis this ratio is itself the specific character. Hence the great importance of the atomic ratio in mineralogy, and it is evident how easily it can be calculated when the symbol of the mineral is given; on the other hand, from the ratio we can as easily construct the general formula of the mineral. Thus in the case of Garnet the ratio between the dyad, hexad, and tetrad radicals is $3 \times II : 1 \times VI : 3 \times IV = 6 : 6 : 12$, or $1 : 1 : 2$, which is evidently expressed in its simplest terms by the symbol above.

In works on mineralogy the atomic ratio is given for each of the native silicates, and in any case this ratio is easily deduced from the results of analysis by simply extending the method for finding the symbol of a body whose molecular weight is unknown (page 62). Having obtained the several quotients which represent the relative number of atoms on the supposition that the molecular weight is 100, we next multiply each of these quotients by the quantivalence of the respective radicals. Lastly, we add together these products for each class of replacing radicals, and compare the several sums thus obtained. For example, an actual analysis of the Bohemian Garnet (Pyrope) gave the following results:—

Si	19.30	or	SiO_2	41.35
$[Al_2]$	11.92	"	Al_2O_3	22.35
Fe	7.73	"	*FeO*	9.94
Mn	2.01	"	*MnO*	2.59
Mg	9.00	"	*MgO*	15.00
Ca	3.77	"	*CaO*	5.29
Cr	3.19	"	*CrO*	4.17
O	43.77			
	100.69			100.69

Dividing now each per cent by the atomic weight of the radical, and multiplying by its quantivalence, we obtain the following numbers:—

Si	$(19.30 \div 28) \times 4 = 2.76$	2.76
$[Al_2]$	$(11.92 \div 54.8) \times 6 = 1.31$	1.31
Fe	$(7.73 \div 56) \times 2 = 0.27$	
Mn	$(2.01 \div 55) \times 2 = 0.07$	
Mg	$(9.00 \div 24) \times 2 = 0.75$	
Ca	$(3.77 \div 40) \times 2 = 0.19$	
Cr	$(3.19 \div 52.2) \times 2 = 0.12$	1.40

whence we deduce the ratio,

$$1.40 : 1.31 : 2.76, \quad \text{or} \quad 1 : 1 : 2 \text{ nearly.}$$

This ratio, although not exact, is as near the theory as we can expect, considering the material and methods used, and is as near as we usually obtain.

There is an uncertainty in the results of all calculations of this kind, which arises from the fact that we have no sure guide in selecting the radicals to be grouped together. Although it is true in general that replacements are limited to radicals of the same atomicity, yet most mineralogists admit that radicals of the form $[R_2]^{\text{IV}}$ may replace $3\,R^{\text{II}}$, and some go so far as to reckon a part of the Si among the basic radicals. Hence our results are to a certain extent arbitrary, and in many cases give no satisfactory information as to the constitution of the mineral analyzed; but by deducing the atomic ratio according to the rule just given, we in all instances reduce the results, as it were, to the simplest terms, and bring them into a form in which they can be most conveniently compared with each other.

It is usual in works on mineralogy to present the results of analysis on the old dualistic plan, as if the mineral were formed by the union of various basic anhydrides with silicon. Starting with such data, however, it is not necessary to calculate the per cent of each radical in the assumed anhydrides before applying the above rule, because by dividing the per cent of each anhydride by its molecular weight we shall obviously obtain the same quotients as before. For example, in the analysis of Garnet cited above, where the data are given in both forms, we have

$$\overset{28}{Si} : \overset{60}{SiO_2} = 19.30 : 41.35, \quad \text{or} \quad 19.30 \div 28 = 41.35 \div 60;$$

and so for each of the other values.

In the symbols of the silicates as formerly written, on the dualistic plan, the atoms of oxygen were necessarily apportioned among the different radicals in proportion to their quantivalence, although this fundamental distinction between them was itself overlooked. Thus, the general symbol of Garnet would be written, dualistically,

$$3\,RO, R_2O_3, 3\,SiO_2,$$

and it is evident that the number of oxygen atoms is in each case a measure of the *relative* atomicities of the radicals with which they are associated. Hence the *atomic ratio* might also be found by comparing together the quantities of oxygen which the several assumed oxides

contain, and this is the manner in which the calculation was formerly made. Hence, also, the *atomic ratio* has been called the *oxygen ratio*, and was long used in mineralogy before its true meaning was understood. But although the old method gives the same results as the new, it is not in harmony with our modern theories, and is practically less simple. Moreover, the principle is far more general than the old method would imply, and may be used with all classes of compounds, as well as with those in which the radicals are cemented together by oxygen. Furthermore, it is sometimes useful to compare the atomic ratios of the complex radicals which may be assumed to exist in different minerals, and interesting relations may frequently be discovered in this way which the old method would entirely overlook.

427. **Silicic Sulphide,** SiS_2. — When the vapor of CS_2 is passed over a mixture of silica and carbon intensely ignited, this compound is deposited in the colder part of the tube in "long, white, silky, flexible, asbestiform needles." It can be volatilized in a current of dry gas; but in contact with moist air, or when heated in aqueous vapor, it rapidly decomposes, the products being H_2S and amorphous silica, the latter of which retains the form of the sulphide. It undergoes a similar decomposition in contact with liquid water, but the silica formed dissolves completely, and the solution, when concentrated, yields the same singular vitreous hydrate, resembling Opal, described above.

428. **Silicic Fluoride,** SiF_4, is a colorless gas (Sp. Gr. = 52) which can only be reduced to the liquid state by great pressure and cold. It is easily prepared by the reaction

$$(SiO_2 + 2\,CaF_2 + 2\,H_2SO_4) = 2\,(CaSO_4 . H_2O) + SiF_4. \quad [364]$$

When brought in contact with the air, it is at once decomposed by aqueous vapor, and forms dense fumes. Passed into water, it is absorbed in large quantities, and the products are silicic hydrate and hydro-silicic fluoride.

$$(3\,SiF_4 + 4\,H_2O + Aq) = H_4SiO_4 + 2\,(2\,HF . SiF_4 + Aq). \quad [365]$$

The same solution can also be obtained by dissolving silica in hydrofluoric acid. It forms, when saturated, a very sour, fuming liquid, which evaporates at 40° in a platinum vessel without leaving any residue. Hence a very simple way of testing the purity of silica.

The solution of hydro-silicic fluoride acts as a strong acid. It dissolves iron or zinc with the evolution of hydrogen, and decomposes

many metallic oxides, hydrates, and carbonates, forming definite salts. It is therefore frequently called silico-fluoric acid (H_2SiF_6), and its salts are named silico-fluorides. The potassium salt, K_2SiF_6, and the barium salt, $BaSiF_6$, are both sparingly soluble in water, and may therefore be readily obtained by precipitation. Moreover, since the corresponding sodium and strontium salts are much more soluble, this reagent may be used to distinguish potassium from sodium, but more especially barium from strontium. Several of the silico-fluorides may be readily crystallized.

Ammonic Silico-fluoride,	$(NH_4)_2SiF_6 . xH_2O$
Cupric Silico-fluoride,	$CuSiF_6 . 7H_2O$
Manganous Silico-fluoride,	$MnSiF_6 . 7H_2O$

429. **Silicic Chloride**, $SiCl_4$, is formed by passing a current of chlorine gas through an intimate mixture of silica and carbon heated intensely in a porcelain tube.

$$SiO_2 + C_2 + 2\,Cl\text{-}Cl = 2\,CO + SiCl_4. \qquad [366]$$

It is a colorless, volatile liquid (*Sp. Gr.* 1.52), boiling at 50°, and is decomposed by water into hydrochloric acid and silicic hydrate. **Sp. Gr.** of vapor 5.94. It is also slowly decomposed by H_2S.

$$SiCl_4 + H_2S = SiCl_3,Hs + HCl. \qquad [367]$$

The new product is a colorless liquid, boiling at 96°, and yielding a vapor whose **Sp. Gr.** = 5.78.

When the vapor of $SiCl_4$ is passed through a white-hot porcelain tube, it undergoes a partial oxidation, and is in part converted into an oxychloride,

$$2\,SiCl_4 + O = Si_2OCl_6 + Cl\text{-}Cl, \qquad [368]$$

the oxygen required coming from the glazing of the tube. This compound is also a colorless fuming liquid, resembling the chloride. It boils at 138°, and has **Sp. Gr.** = 10.05.

430. **Silicic Bromide**, $SiBr_4$, may be formed in a similar way, and closely resembles the chloride, but is less volatile, boiling at 153°, and crystallizing at from 12° to 15°. **Sp. Gr.** of vapor 12.05. The compound $SiCl_3I$, **Sp. Gr.** = 7.25, is also known.

431. **Silicic Iodide**, SiI_4, is a colorless crystalline solid, melting at 120°.5, and boiling at about 290°. **Sp. Gr.** of vapor 19.12. It

crystallizes in regular octahedrons, and is obtained by passing iodine vapor in a stream of CO_2 over ignited silicon.

432. **Silicic Hydride.** SiH_4. — One of the silicic ethers (§ 435), when heated with sodium, furnishes this remarkable compound in a pure condition.

$$4\,((C_2H_5)_3{\equiv}O_3{\equiv}SiH) = 3\,((C_2H_5)_4{\equiv}O_4{\equiv}Si) + \mathrm{SiH_4}. \qquad [369]$$

The sodium induces the chemical change by its mere presence. The composition of silicic hydride has been determined by the following reaction: —

$$\mathrm{SiH_4} + (2\,K\text{-}O\text{-}H + H_2O + Aq) = (K_2{=}O_2{=}SiO + Aq) + 4\,\mathrm{H\text{-}H}. \qquad [370]$$

It is a colorless gas, which inflames at a very low temperature (under some conditions spontaneously), and yields when burnt silicic anhydride and water.

433. **Silicic Hydrochloride,** $SiHCl_3$, is a colorless inflammable liquid, obtained by passing HCl over ignited silicon. It has **Sp. Gr.** = 4.64, and may be regarded as the chloride of the radical $(SiH){\equiv}Cl_3$, corresponding to chloroform, $(CH){\equiv}Cl_3$, among the compounds of carbon. The corresponding bromine and iodine compounds are also known. When mixed with water these substances are decomposed, and a voluminous white powder is formed, which has been called Leukon.

$$2\,SiHCl_3 + 3\,H_2O = (SiOH)_2{=}O + 6\,HCl. \qquad [371]$$

Leukon dissolves in the alkaline hydrates or carbonates, yielding an alkaline silicate and evolving hydrogen. It also decomposes water, and acts in general as a reducing agent.

434. **Silicic Ethide,** $Si(C_2H_5)_4$, and **Silicic Methide,** $Si(CH_3)_4$, are two colorless volatile liquids, prepared by heating $SiCl_4$ with zinc ethide and zinc methide in sealed tubes. They boil respectively at 30° and 153°, and their vapors have a **Sp. Gr.** of 3.08 and 5.13. Also another compound has been described whose symbol may be written $O{=}Si_2{\equiv}(C_2H_5)_6$.

435. **Silicates of the Organic Radicals, or Silicic Ethers.** — A large number of these compounds have been prepared, containing the radicals methyl, ethyl, and amyl, either singly or associated in different combinations. They are all colorless volatile liquids, highly combustible, and having for the most part an ethereal odor. We give in the following table the symbols, the boiling points, and the vapor densities

of several of the most interesting ethers, and of the chlorhydrines (§ 280) derived from them.

	Sp. Gr. of Liquid.	Boiling Point.	Vapor Density.	
			Obs.	Calc.
$(CH_3)_4{\equiv}O_4{\equiv}Si$	1.059	121° – 122°	5.38	5.26
$(CH_3)_3{=}O_3{=}Si\text{-}Cl$	1.195	114°.5 – 115°	5.58	5.42
$(CH_3)_2{=}O_2{=}Si{=}Cl_2$	1.259	98° – 103°	5.66	5.57
$(CH_3)\text{-}O\text{-}Si{\equiv}Cl_3$		82° – 86°	5.66	5.73
$(CH_3)_6{\equiv}O_6{\equiv}Si_2O$	1.144	201° – 202°.5	9.19	8.93
$(C_2H_5)_4{\equiv}O_4{\equiv}Si$	0.968	165° – 166°	7.32	7.27
$(C_2H_5)_3{=}O_3{=}Si\text{-}H$		134°		5.68
$(C_2H_5)_3{=}O_3{=}Si\text{-}Cl$	1.048	157°	7.05	6.81
$(C_2H_5)_2{=}O_2{=}Si{=}Cl_2$	1.440	137°	6.76	6.54
$(C_2H_5)\text{-}O\text{-}Si{\equiv}Cl_3$	1.291	104°	6.38	6.22
$(C_2H_5)_6{\equiv}O_6{\equiv}Si_2O$	1.020		12.02	11.86
$(C_2H_5)_3,(C_2H_5O){\equiv}O_4{\equiv}Si$		190°		7.69
$(CH_3)_2,\ (C_{25}H)_2{\equiv}O_4{\equiv}Si$	1.004	143° – 146°	6.18	6.23
$(CH_3),\ (C_2H_5)_3{\equiv}O_4{\equiv}Si$	0.981	155° – 157°		6.72
$(C_2H_5)_2,(C_5H_{11})_2{\equiv}O_4{\equiv}Si$	0.915	245° – 250°		10.12
$(C_2H_5),\ (C_5H_{11})_3{\equiv}O_4{\equiv}Si$	0.913	280° – 285°		11.57

The following equations illustrate some of the reactions by which these compounds have been prepared :—

$$4\,C_2H_5\text{-}O\text{-}H + SiCl_4 = (C_2H_5)_4{\equiv}O{\equiv}Si + 4\,HCl. \quad [372]$$

$$3\,((C_2H_5)_4{\equiv}O_4{\equiv}Si) + SiCl_4 = 4\,(C_2H_5)_3{=}O_3{=}SiCl. \quad [373]$$

$$(C_2H_5)_4{\equiv}O_4{\equiv}Si + SiCl_4 = 2\,(C_2H_5)_2{=}O_2{=}SiCl_2. \quad [374]$$

$$(C_2H_5)_3{=}O_3{=}SiCl + C_5H_{11}\text{-}O\text{-}H = (C_2H_5)_3,(C_5H_{11}){\equiv}O_4{\equiv}Si + HCl. \quad [375]$$

$$3\,(C_2H_5)\text{-}O\text{-}H + SiHCl_3 = (C_2H_5)_3{=}O_3{=}SiH + 3\,HCl. \quad [376]$$

$$6\,(C_2H_5)\text{-}O\text{-}H + Si_2OCl_6 = (C_2H_5)_6{\equiv}O_6{\equiv}Si_2O + 6\,HCl. \quad [377]$$

In general, these reactions may be obtained by simply heating together the several factors, enclosed if necessary in sealed tubes. The process is usually complicated by accessory changes, and a mixed product results, which must be purified by repeated fractional distillation.

QUESTIONS AND PROBLEMS.

1. Compare the properties of silicon in its different conditions with those of boron.

2. Make a table illustrating the relations of the possible hydrates of silica.

3. Required the general formula of the following mineral species when the atomic ratios are given in the table : —

	$\overset{I}{R}$	$\overset{II}{R}$	VI $[R_2]$	Si	H	Formula required.
Anorthite		1	3	4		$\overset{II}{R},[R_2]^{vi}O_8{}^{vi}Si_2$
Sarcolite		1	1	2		$\overset{II}{R_3}[R_2]^{xii}O_{12}{}^{xii}Si_2$
Epidote		1	2	3		$\overset{II}{R_6},[R_2]_4{}^{xxxvi}O_{26}{}^{xxvi}Si_3$
Vesuvianite		3	2	5		$\overset{II}{R_{18}},[R_2]_4{}^{ix}O_{60}{}^{ix}Si_{15}$
Leucite	1		3	8		$\overset{I}{R_2},[R_2]^{vi}O_8{}^{vi}Si_4O_4$
Beryl		1	1	4		$\overset{II}{R_3},[R_2]^{xii}O_{12}{}^{xii}Si_6O_6$
Iolite		1	3	5		$\overset{II}{R_2},[R_2]_2{}^{xvi}O_{16}{}^{xvi}Si_2O_7$
Oligoclase	1		3	10		$\overset{I}{R_2},[R_2]^{vi}O_8{}^{vi}Si_8O_8$
Natrolite	1		3	6	2	$\overset{I}{R_2},[R_2]^{vi}O_8{}^{vi}Si_2O_2 . 2H_2O$
Analcime	1		3	8	2	$\overset{I}{R_2},[R_2]^{vi}O_8{}^{vi}Si_4O_4 . 2H_2O$
Harmotome		1	3	10	5	$\overset{II}{R},[R_2]^{vi}O_8{}^{vi}Si_5O_5 . 5H_2O$
Stilbite		1	3	12	6	$\overset{II}{R},[R_2]^{vi}O_8{}^{vi}Si_6O_6 . 6H_2O$

The number of atoms of oxygen, which form the vinculum in each of the above formulæ, is always necessarily equal to the total atomicity of all the basic radicals, and as many atoms of oxygen are associated with the acid radical as are required to complete the molecule. The last evidently serve to bind together the atoms of silicon when they are in excess over the number required to neutralize the base (§ 299). The precise form we give to the symbols is in great measure arbitrary, and must be determined from many circumstances, which do not influence the results of analysis ; and the great advantage of expressing these results in the form of an atomic ratio is found in the fact that they are thus reduced to the simplest terms, and exhibited independently of all hypothesis, leaving each student to construct the formulæ according to his own theoretical conceptions.

4. Represent the constitution of Anorthite, Sarcolite, and Beryl by graphic symbols.

5. In the following table the percentage composition of a number of native silicates is given on the usual plan, as if they were composed of basic anhydrides and silica. It is required in each case to deduce the atomic ratio and construct the formula.

	Na_2O	K_2O	Li_2O	FeO	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	H_2O	Ratio.
Wollastonite					48.3				51.7		1:2
Pyroxene				8.0	24.9	13.4			53.7		1:2
Spodumene			6.4				29.4		64.2		1:2
Petalite	1.2		3.3				17.8		77.7		1:4
Forsterite						57.14			42.86		1:1
Iron Garnet					17.3	12.4		33.1	37.2		1:1:2
Zoisite					37.3		22.8		39.9		1:1:2
Ilvaite				31.5	12.3			23.4	32.8		3:2:5
Sarcolite	4.1				33.4		22.8		39.7		1:1:2
Andesine	6.53	1.08			5.77	1.08	24.28	1.58	59.60		1:3:8
Analcime	14.1						23.3		54.4	8.2	1:3:8:2
Heulandite					9.2		16.9		59.1	14.8	1:3:12:5

6. It was formerly supposed that the symbol of silica was Si_2O_3, corresponding to that of boric oxide, B_2O_3, when $Si = 21$ and $O = 16$. What facts can you adduce in support of the symbol adopted in this book?

7. Deduce the atomic weight of silicon from the data of § 435, according to the principle of § 20. It is assumed that the percentage composition of the various compounds has been accurately determined by analysis.

8. Point out the analogies between the properties of silicic fluoride and chloride, and those of the corresponding compounds of boron.

9. Compare the chemical qualities of silicon with those of the elements immediately preceding it in our classification. To which element is it more closely allied?

10. Compare the chemical qualities of silicon with those of carbon, and illustrate by examples the analogies between those elements.

11. Point out the examples of chlorhydrines in the table of § 435.

12. Describe and illustrate by reactions the methods by which the silicic ethers and chlorhydrines are prepared.

DIVISION XXX.

436. **CARBON.** $C = 12$. — Quadrivalent. One of the most widely diffused and one of the most important elements in the scheme of terrestrial nature. United to the three aeriform elements, oxygen, hydrogen, and nitrogen, it forms the chief solid substratum of all organized structures. Combined with oxygen it forms the carbonic dioxide of the atmosphere, which is the food of the whole vegetable world. In a nearly pure condition, or combined with hydrogen, it is found in the earth's strata, forming those deposits of coal and petroleum which are such great stores of light, heat, and motive power (§ 65). Lastly, it is an essential constituent of the limestones and Dolomites, which constitute an important part of the rocky crust of the globe (§§ 189, 221). The elementary substance is found in nature in three very different conditions, namely, coal, graphite, and diamond.

437. **COAL.** — All organized tissues, and many other carbonaceous materials, when heated without free access of air, are charred; that is, volatile products are driven off, and more or less of the carbon is left behind in an uncombined condition. Common charcoal, animal charcoal, lamp-black, ivory-black, etc. are all artificial products of this kind, and mineral coal is the charred remains of the rank vegetation of an early geological epoch. Since carbon is, under all circumstances, infusible and non-volatile, coal frequently retains the structure of the organic tissue from which it was derived, and this element may therefore be regarded as the skeleton of all organic forms, which in the process of growth gather around this solid nucleus the elements of air and water. The great porosity of many kinds of coal, which results from its organic structure, renders it a powerful absorbent both of aeriform and liquid materials, and hence the use of wood charcoal as a disinfecting, and of bone-black as a decolorizing agent. The ready combustibility of coal is, however, the most characteristic and important, as it is the most familiar quality of this variety of carbon, which is peculiarly adapted for its all-important uses as fuel, not only on account of its high calorific power, but also because it retains its solid condition at the highest furnace heat, and because the product of its combustion is an invisible innocuous gas, the appropriate food of plants. In its more porous conditions coal is a non-conductor of heat

and electricity, has a low specific gravity and a high specific heat, both varying, however, in different varieties between quite wide limits.

438. **Graphite** has usually a foliated structure, and is found occasionally in small six-sided tables belonging to the third system, but it is also met with in compact amorphous masses. From its frequent association with crystalline minerals, evidently the products of aqueous action, we naturally infer that it must have been formed in a similar way; but the nature of the process is not understood. Graphite is very soft, leaving a black shining streak on paper, and has a *Sp. Gr.* = 1.209. It is practically incombustible, although it burns slowly in an oxyhydrogen flame, or when ignited in a current of oxygen gas. It has a metallic lustre, and, since it also conducts electricity nearly as well as the metals, it has been called Metallic Carbon.

The carbon which separates from some varieties of cast-iron when the molten metal slowly cools is in the condition of graphite, and the cavities in iron slags are sometimes lined with crystalline plates of the same material. Moreover, when coal is intensely heated in a close vessel, it acquires the characteristic lustre and conducting power of the same mineral, and a similar product is formed in the iron retorts in which illuminating-gas is manufactured. Ordinary coke also sometimes approaches the same condition. All these materials, however, are usually very hard, and thus differ from true graphite; but under the intense heat of the electric arc, the carbon points of the electric lamp often acquire all the characteristics of the native mineral.

Graphite may be obtained in a state of minute subdivision by heating with strong sulphuric acid the coarsely pulverized mineral, previously mixed with one fourteenth of its weight of potassic chlorate, and, after washing with water and drying, igniting the residue. If this process is many times repeated the graphite is converted into a yellow crystalline product, which has been called graphitic acid, and which has been regarded as a peculiar compound of the graphitoidal condition of carbon. Analysis gives the symbol $C_{11}H_4O_5$.

439. **DIAMOND.** — This well-known gem is also a crystalline condition of carbon. It affects the forms of the monometric system, and may be cleaved in directions which are parallel to the faces of the regular octahedron. Its peculiar brilliancy is due to a very high refractive and dispersive power united to a strong lustre called Adamantine. The effect is greatly increased by the lapidary, who cuts numerous facets on the gem, which reflect and disperse the light in

various directions. Diamond is the hardest substance known, and can therefore only be cut with its own powder. Rough or small stones called "Bort Diamonds," which are otherwise valueless, are pounded up and used for this purpose. The mineral called Carbonado is a porous and massive form of impure diamond, which is used for forming the points of rock-boring tools. On account of its great hardness diamond crystals are used for cutting glass, and the convexity of the faces enables them to bear the necessary pressure without breaking. The diamond burns at a high temperature much more readily than graphite, and in an atmosphere of pure oxygen sustains its own combustion, yielding CO_2 like all other forms of carbon. It is a poor conductor of electricity, but when intensely heated in the voltaic arc it suddenly acquires this power, becomes specifically lighter, and is converted into a kind of coke. It is found in alluvial soil at only a few localities, chiefly in India, Borneo, and Brazil.

It will thus be seen that carbon presents the most remarkable example of allotropism which has been observed in nature, and the essential differences between the three states appear chiefly in the form, density, and capacity for heat, (compare page 46,) which we sum up in the table below:—

	Crystalline Form.	*Sp. Gr.*	*Sp. Ht.*
Wood Charcoal,	Amorphous,	0.300	0.2415
Graphite,	Hexagonal,	2.229	0.2017
Diamond,	Isometric,	3.529	0.1469

In all these forms carbon is chemically the same, and yields the same product (CO_2) when burnt. It is not only non-volatile and infusible, but does not even soften in the hottest fire; although in the experiments of Despretz, with a voltaic battery of intense energy, it appears to have undergone incipient fusion, and to have been partially volatilized. Lastly, although combustible at a high temperature, yet under ordinary conditions carbon effectually resists, and for an indefinite period, the action of all atmospheric agents, and its uses for fuel on the one hand, and for printing-ink on the other, are remarkable illustrations of the singular twofold aspects of this element in the economy of nature.

We have no knowledge of the origin of the diamond; but minute crystals are said to have been produced artificially by decomposing bone oil by metallic lithium at a high temperature under great pres-

ure. The bone oil and lithium, mixed with paraffine spirit, were heated to a red heat in a closed iron tube for fourteen hours.

CARBON AND OXYGEN, or SULPHUR.

440. **Carbonic Dioxide,** CO_2. — With this aeriform product of ordinary combustion the student must have already become familiar. Although a gas under ordinary conditions, it can be condensed by pressure and cold to a colorless limpid liquid, which freezes by its own evaporation to a light flocculent solid, outwardly resembling snow, a condition in which it is used to produce a great degree of cold. As a gas it is distinguished by the absence of all those qualities which affect the senses, and hence, although playing such an important part in nature, it escaped notice until the year 1757, when it was first discovered by Dr. Black. It is not only a product of the combustion of all carbonaceous materials, and of the slow oxidation of organic tissues called decay, but it is also one of the chief products of respiration, and of the other processes of animal life. Carbonic dioxide is likewise formed during fermentation, and is the cause of the effervescence in all fermented liquids. It is a product of volcanic action, and is copiously evolved from the earth in many localities, especially in volcanic districts. As it is much heavier than the air, Sp. Gr. = 1.529, it not unfrequently collects in wells, mines, and caverns, and it is the chokedamp which has occasioned so many serious accidents; for although not poisonous, properly speaking, the free secretion of carbonic dioxide from the body is an essential condition of life, and this is arrested as soon as the amount in the atmosphere exceeds a small per cent.

Although an immense flood of carbonic dioxide is being constantly poured into the atmosphere from the various sources just enumerated, yet in the beautiful balance of creation the plant restores the equilibrium which these causes tend to disturb. This product of animal life, of decay, and of combustion is the food of the vegetable world, and, as has been stated (§ 69), the sun's rays acting on the leaves of the plant undo the work of destruction, and while the plant fixes the carbon in its tissues, the oxygen is restored to the atmosphere. While the plant is an apparatus of reduction, the animal is an apparatus of combustion, in which the carbon it receives with its food is burnt in each act of life, and every breath carries back carbonic dioxide to the atmosphere, ready to be reabsorbed by the plant, and repass through the phases of organic life.

Water dissolves very nearly its own volume of carbonic dioxide gas (§ 58), and this important agent is as universally diffused through the waters of the globe as it is through the atmosphere, and sustains the same intimate relations to the plants and animals which inhabit the water as it does to those which live in the air. Moreover, in this condition of solution carbonic dioxide is a very active and important agent in the mineral kingdom, exerting a powerful solvent action on many minerals which would be otherwise unaffected by water, and thus causing extensive geological changes. (§§ 189, 221, and Prob. 66, page 396.)

Although the solution of CO_2 in water acts in all respects like a simple solution (§ 59), yet there are reasons for regarding it as a solution of carbonic acid, and writing its symbol $(H_2{=}O_2{=}CO + Aq)$. It has an acid reaction (§ 40), and dissolves iron with the evolution of hydrogen gas (§ 266). Moreover, it neutralizes many basic hydrates, and such reactions are most simply regarded as examples of direct metathesis, thus: —

$$(Ca{=}O_2{=}H_2 + H_2{=}O_2{=}CO + Aq) = Ca{=}O_2{=}CO + (2\,H_2O + Aq). \quad [378]$$

Carbonic acid is a weak dibasic acid, and forms two distinct classes of salts, the most important of which have already been described (§§ 144, *et seq.*), and, as may be inferred from what has been said, carbon is next to silicon the most abundant acid radical in the mineral kingdom.

The quantity of CO_2 formed by the burning of a known weight of carbon can be collected and weighed with the greatest accuracy, and it was thus that the atomic weight of carbon was determined. Dumas found in a series of very accurate experiments that 100 parts of pure carbon yield exactly 366.66+ parts of CO_2.

441. **Carbonic Monoxide**, CO, is, like CO_2, a colorless gas, but contains in the same volume only one half as much oxygen, and its molecules, not being saturated, act as powerful dyad radicals (§ 29). The gas is devoid of odor and taste, is very poisonous, is but slightly soluble in water, and can be condensed to the liquid state only with great difficulty. When ignited it burns with a blue flame, and when in contact with heated metallic oxides it acts as a powerful reducing agent, in each case eagerly absorbing more oxygen without changing its volume. It is formed abundantly in all furnaces and grates whenever the first product of combustion, always CO_2, subsequently passes

through a mass of ignited carbonaceous combustible, and it plays an important part in many metallurgical processes, not unfrequently occasioning a great loss of heat by escaping combustion. It is also formed, together with hydrogen, when steam is passed over ignited coal, and it is a chief ingredient in the so-called water gas.

Carbonic monoxide may be obtained in a pure condition by a number of chemical reactions, of which the following is the most available :—

$$\underset{\text{Potassic Ferrocyanide.}}{K_4{\equiv}(FeC_6N_6)} + 6\,H_2{=}O_2{=}SO_2 + 6\,H_2O =$$

$$Fe{=}O_2{=}SO_2 + 2\,K_2{=}O_2{=}SO_2 + 3\,(NH_4)_2{=}O_2{=}SO_2 + 6\,\text{©©}. \quad [379]$$

So, also, when oxalic acid is dehydrated, — best by heating the crystals with concentrated sulphuric acid, — it breaks up with evolution of CO_2 and CO, which are set free in equal volumes, and the CO may be isolated by passing the gas through a solution of caustic alkali which absorbs the CO_2.

$$H_2{=}O_2{=}C_2O_2 - H_2O = \text{©©}_2 + \text{©©}. \quad [380]$$

In theoretical chemistry CO is chiefly interesting as an important acid radical, and when acting in this capacity it is usually known as carbonyl. It is the acid radical not only in the normal carbonates, but also in almost all of the organic acids. The following beautiful synthetical reaction, obtained by simply heating carbonic monoxide gas with potassic hydrate, illustrates the relations of this radical to an important class of organic acids.

$$K\text{-}O\text{-}H + CO = \underset{\text{Potassic Formate.}}{K\text{-}O\text{-}(CO\text{-}H)}. \quad [381]$$

Under the influence of direct sunlight, carbonic monoxide combines directly with chlorine, forming $CO{=}Cl_2$, called phosgene gas. This compound is at once decomposed both by water and ammonia (NH_3), and in each of the resulting reactions the radical CO evidently retains its integrity.

$$CO{=}Cl_2 + H_2O = 2\,HCl + CO_2. \quad [382]$$

$$CO{=}Cl_2 + 4\,H_3N = \underset{\text{Urea.}}{H_2,H_2{\equiv}N_2{=}CO} + 2\,NH_4Cl. \quad [383]$$

442. **Oxalic Acid.** $H_2{=}O_2{=}C_2O_2 . 2\,H_2O$. — The anhydride of this acid, C_2O_3, has never been obtained, and the acid itself forms the first term of an important series of compounds, all of which contain hydrogen. Strictly, therefore, it cannot be classed with the simple com-

pounds of carbon and oxygen, but nevertheless it is best studied in this connection.

The calcic and potassic salts of oxalic acid are found in the juices of many plants, and when organic bodies are oxidised by nitric acid, or similar agents, this acid is one of the most common products. It is made in the arts by the action of nitric acid on sugar or starch, and also by heating sawdust with caustic potash.

Oxalic acid easily crystallises in prisms which have the composition indicated above. These crystals lose their water of crystallisation at 100°, and at 160° the body itself is broken up, the products being carbonic dioxide and formic acid; but the greater part of the last is still further decomposed into water and carbonic monoxide, and a portion of the oxalic acid always sublimes unchanged.

$$C_2H_2O_4 = CH_2O_2 + CO_2, \quad \text{and} \quad CH_2O_2 = H_2O + CO. \quad [384]$$

When, however, the acid is heated with glycerine, the reaction is arrested at the first stage, and yields the equivalent quantity of formic acid.

Oxalic acid is both diatomic and dibasic. Thus we have, —

Normal Potassic Oxalate,	$K_2{\cdot}O_2{\cdot}C_2O_2.H_2O$
Acid Potassic Oxalate (Salt of Sorrel),	$H,K{\cdot}O_2{\cdot}C_2O_2.H_2O$
Super-acid Potassic Oxalate,	$H,K{\cdot}O_2{\cdot}C_2O_2.H_2{\cdot}O_2{\cdot}C_2O_2.2H_2O$

The last is usually regarded as a molecular compound. With the exception of the alkaline salts, the oxalates are, as a rule, insoluble or difficultly soluble in water, and on the great insolubility of calcic oxalate several important analytical processes depend.

Calcic oxalate, when heated to not too high a temperature, is converted into calcic carbonate.

$$Ca{\cdot}O_2{\cdot}C_2O_2 = Ca{\cdot}O_2{\cdot}CO + CO. \quad [385]$$

When, however, the acid itself is heated with an excess of lime, we obtain a somewhat different result.

$$H_2{\cdot}O_2{\cdot}C_2O_2 + 2CaO = 2Ca{\cdot}O_2{\cdot}CO + H{-}H. \quad [386]$$

Oxidising agents convert oxalic acid into CO_2 (Prob. 18, page 393) by removing hydrogen.

$$H_2{\cdot}O_2{\cdot}C_2O_2 + O = H_2O + 2CO_2. \quad [387]$$

Substances having a strong attraction for water transform the acid into CO_2 and CO [380].

Argentic oxalate, when heated, is resolved with explosion into metallic silver and CO_2.

$$Ag_2{=}O_2{=}C_2O_2 = Ag\text{-}Ag + 2CO_2. \qquad [388]$$

On the other hand, when an amalgam of potassium is heated in an atmosphere of CO_2, the gas is absorbed, and potassic oxalate results.

$$K\text{-}K + 2CO_2 = K_2{=}O_2{=}C_2O_2. \qquad [389]$$

These reactions all justify the rational symbol assigned to oxalic acid, and by writing the symbol as in the margin the relation of the atoms is made more evident. We thus see that dry oxalic acid may be regarded as formed by the union of two atoms of the compound radical $(Ho\text{-}CO)$-, held together by one affinity of each of the carbon radicals, which, when not thus satisfied, may join the radical to any other group of atoms that is in the condition to hold it. This radical is called carboxyl, and dry oxalic acid is evidently the corresponding radical substance. Carboxyl, as is evident, is not only univalent, but also monobasic, and therefore must transform any group of atoms to which it is united into an acid. Moreover, the basicity of such an acid will be measured by the number of atoms of carboxyl which it contains. Now nearly all the so-called organic acids may be regarded as compounds of carboxyl with the different hydrocarbon radicals. Those containing one atom of carboxyl are monobasic, those containing two atoms are dibasic, those containing three are tribasic. Carboxyl, however, must itself be regarded as a compound of carbonyl with hydroxyl, and thus we arrive at this important general principle: *The basicity of an organic acid is determined by the number of atoms of Ho which it contains associated with carbonyl.* Moreover, it now appears why the basicity may be less than the atomicity; for the last is measured by the *total* number of *Ho* atoms present, however united to the nucleus of the compound (§ 44). But while the hydrogen of all the *Ho* atoms in a compound may be displaced by very positive metals, or compound radicals of either class, we can only displace *by double decomposition with bases* the hydrogen of those atoms which are associated with carbonyl.

$H\text{-}O\text{-}C{=}O$
$H\text{-}O\text{-}C{=}O$

The explanation of this important principle seems to be, that, while a strong positive metal, such as sodium, will, like a powerful magnetic pole, increase the attraction of the point of affinity to which it is opposed, and thus give to it an energy it would not otherwise possess,

yet in the ordinary metathetical reactions the atoms of hydrogen cannot be displaced unless they are in a polar condition, such as is determined by their association with carbonyl.

CARBON AND SULPHUR.

443. **Carbonic Disulphide.** CS_2. — Charcoal burns in an atmosphere of sulphur vapor with almost as much energy as in oxygen, forming a colorless gas, which at the ordinary temperature of the air condenses to a very volatile liquid, distinguished for its very great refractive and dispersive power, and much used in the arts as a solvent of phosphorus, sulphur, and caoutchouc. The compound CS has never been obtained in a free state, but the following reactions indicate that it exists as an acid radical in certain sulphur salts (§ 39).

$$K_2S + CS_2 = K_2{=}S_2{=}CS. \qquad [390]$$

$$(Pb{=}O_2{=}(NO_2)_2 + K_2{=}S_2{=}CS + Aq) = Pb{=}S_2{=}CS + (2\,K\text{-}O\text{-}NO_2 + Aq). \qquad [391]$$

$$Pb{=}S_2{=}CS + (H_2S + Aq) = PbS + (H_2{=}S_2{=}CS + Aq). \qquad [392]$$

CARBON AND NITROGEN.

444. **Cyanogen.** CN. — Although carbon will not combine directly with nitrogen, yet when heated in an atmosphere of this gas, and in the presence of a strong alkaline base, the two elements unite with the alkaline metals, and the resulting product contains the compound radical CN, with which the student is already familiar, under the name of Cyanogen.

$$K_2{=}O_2{=}CO + 4\,C + N{\equiv}N = 2\,K\text{-}CN + 3\,CO. \qquad [393]$$

Like carbonyl, cyanogen is a strong negative or acid radical, and we need admit no other acid radical than these two "in investigating the whole range of organic compounds."* In many of its chemical rela-

* There is, however, a class of acids, formed by the action of $H_2{=}O_2{=}SO_2$ on various organic substances, in which the radical $(Ho\text{-}SO_2)$- appears to play the same part as the radical carboxyl in the compounds just noticed. Such bodies were formerly said to be copulated, or conjugated, and these terms, though latterly discarded, were not wholly inappropriate.

tions cyanogen closely resembles the elements of the chlorine group, forming many compounds which are analogous to the corresponding chlorides, bromides, and iodides, but in other respects it differs widely from these elements, both on account of its compound nature, and the singularly complex relations of the two elements of which it consists. Its univalent condition is an obvious result of the quantivalence of its two constituents.

445. **Cyanogen Gas,** *CN-CN* or *Cy-Cy*, bears the same relation to the radical *CN* that chlorine gas bears to the element chlorine (§§ 54, 129). It is easily made by heating mercuric cyanide.

$$HgCy_2 = Hg + Cy\text{-}Cy. \qquad [394]$$

At the same time a brown non-volatile product is formed, which is called Paracyanogen. This body is isomeric with the gas, but probably represents a more condensed molecular condition, and is converted wholly into cyanogen when heated in an inert atmosphere.

Cyanogen has been condensed to a liquid, boiling at —20°.7, and freezing below —34°, which is its melting point. The gas is colorless, has a suffocating odor, and is poisonous. It burns with a beautiful flame, which recalls the color of peach-blossoms, and the products of its combustion are CO_2 and $N{\equiv}N$. It dissolves in water, but not so freely as in alcohol. The aqueous solution, moreover, is not permanent, for the cyanogen slowly unites with the elements of water, changing into ammonic oxalate.

$$CN\text{-}CN + 4H_2O = (NH_4)_2{=}O_2{=}C_2O_2. \qquad [395]$$

On the other hand, when ammonic oxalate is heated, the action is reversed, and these facts show how easily carboxyl and cyanogen are convertible. Cyanogen unites directly with potassium, forming *K-CN*.

446. **Hydrocyanic Acid.** *H-CN.* — The anhydrous acid (a combustible and very volatile liquid) is most readily obtained by passing H_2S over $HgCy_2$; but a solution of the acid in water (the Prussic Acid of pharmacy) may be made by distilling potassic cyanide or ferrocyanide with dilute sulphuric acid. It can also be formed by the following very interesting reaction :—

$$CHCl_3 + NH_3 = 3\,HCl + HCN.$$

Hydrocyanic acid has the peculiar odor of bitter almonds, and is intensely poisonous. It is a very unstable body, and undergoes sponta-

neous decomposition, which is greatly accelerated by the action of the light. When diluted with water, and mixed with a mineral acid, it is more permanent, but it is so volatile that even the very dilute acid used in pharmacy rapidly loses strength when exposed to the air.

By absorption of the elements of water, both ammonic oxalate and ammonic formate are slowly produced in the aqueous acid; the first by a reaction similar to [395], and the second thus: —

$$H\text{-}CN + 2H_2O = \underset{\text{Ammonic Formate.}}{NH_4\text{-}O\text{-}(CO\text{-}H)}. \qquad [396]$$

When the vapor of ammonic formate is passed through a red-hot tube, the last reaction is reversed. In like manner, when hydrocyanic acid is mixed with hydrochloric acid (both concentrated), we have

$$H\text{-}CN + HCl + 2H_2O = \underset{\text{Formic Acid.}}{H\text{-}O\text{-}(CO\text{-}H)} + NH_4\text{-}Cl. \qquad [397]$$

447. **Cyanides.** — Hydrocyanic acid reddens litmus feebly, and potassic cyanide has an alkaline reaction. The acid, however, freely dissolves HgO, forming $HgCy_2$, and in a similar way (or more readily by metathesis from potassic cyanide) a large number of metallic cyanides may be obtained. The alkaline cyanides are very soluble in water, and several of the cyanides of the heavier metals, like $HgCy_2$, dissolve to a limited extent. Most of them, however, are insoluble in pure water, but with few exceptions they all dissolve freely in solutions of the alkaline cyanides, with which they form double salts, and solutions of $AgCy$ and $AuCy_3$ in $(KCy + Aq)$ are very much used in the process of electroplating. The double cyanides are a still more definite and numerous class of salts than the simple cyanides. Among them we may cite as examples

$$AgCy\,.\,KCy, \quad \text{and} \quad ZnCy_2\,.\,2KCy.$$

All these cyanides contain cyanogen as such, and, with few exceptions, when heated with dilute hydrochloric acid, they yield HCy, and, if soluble, are violent poisons. There is, however, another class of compounds formed by combining with the alkaline cyanides the cyanides of iron, cobalt, chromium, platinum, and a few of the rarer metals; these compounds do not evolve HCy under the influence of hydrochloric acid, and have not the same deadly character. Moreover, the metals which they contain cannot be displaced by the usual metathetical methods. Hence we have come to the conclusion that these bodies are not simple cyanides of the metals, but contain far more

complex radicals, of which the metals just mentioned form a part. The most important of these compounds are described in the next two sections.

448. **Ferrocyanides.** $R_4^{\equiv}(FeC_6N_6)$ or $R_4^{\equiv}Cfy$. — Potassic ferrocyanide (Yellow Prussiate of Potash), $K_4^{\equiv}Cfy$, is an important commercial product, manufactured on a large scale by fusing nitrogenized animal matter with potassic carbonate and iron filings, lixiviating the resulting mass with water, and crystallizing. The salt forms large yellow, square, tabular crystals, is very much used in dyeing, and is the primary source of all the cyanogen compounds. It may also be made from KCy or HCy by the following reactions: —

$$FeS + 6\,K\text{-}CN = K_4^{\equiv}(FeC_6N_6) + K_2S. \qquad [398]$$

1. $2\,Fe_2O_3 + 3\,FeO + 18\,H\text{-}CN = [Fe_2]_2^{\text{xii}}(FeC_6N_6)_3 + 9\,H_2O.$ [399]

Prussian Blue.

2. $[Fe_2]_2^{\text{xii}}Cfy_3 + (12\,K\text{-}Ho + Aq) =$
$$2\,[Fe_2]^{\equiv}Ho_6 + (3\,K_4^{\equiv}Cfy + Aq). \qquad [400]$$

When fused, the ferrocyanide is partially decomposed, yielding potassic cyanide, which is made in great quantities in this way.

$$K_4^{\equiv}(FeC_6N_6) = 4\,K\text{-}CN + FeC_2 + N\text{-}N. \qquad [401]$$

By previously mixing the ferrocyanide with potassic carbonate a larger product is obtained, but less pure, as potassic cyanide is formed at the same time.

$$K_4^{\equiv}(FeC_6N_6) + K_2{}^{=}O_2{}^{=}CO = 5\,K\text{-}CN + K\text{-}O\text{-}CN + Fe + CO_2. \qquad [402]$$

From the solution of the potassium salt various ferrocyanides are easily prepared by simple metathesis, and several of them have striking and characteristic colors. Thus, when the solution is mixed with hydrochloric acid and ether, hydro-ferrocyanic acid is precipitated.

$$K_4^{\equiv}Cfy + 4\,HCl = H_4^{\equiv}Cfy + 4\,KCl. \qquad [403]$$

With a ferric salt we obtain Prussian Blue (ferric ferrocyanide).

$$(2\,[Fe_2]^{\equiv}Cl_6 + 3\,K_4^{\equiv}Cfy + Aq) =$$
$$[Fe_2]_2^{\text{xii}}Cfy_3 + (12\,KCl + Aq). \qquad [404]$$

Hence the origin of the name Cyanogen (κύανος and γεννάω).

With a ferrous salt the precipitate is white or nearly so, but becomes blue in contact with the air.

$$(Fe''Cl_2 + K_4Cfy_6 + Aq) = \underset{\text{White.}}{K_2Fe''Cfy_6} + (2\,KCl + Aq).$$

$$12\,K_2Fe''Cfy_6 + 3O_2 + O = 2\underset{\text{Blue.}}{[Fe_2'''](Cfy_6)_3} + 6\,K_4Cfy_6 + 2\,Fe_2O_3. \quad [403]$$

With cupric salts we have a red precipitate.

$$(2\,Cu''O_2SO_2 + K_4Cfy_6 + Aq) = Cu_2''Cfy_6 + (2\,K_2''O_2SO_2 + Aq). \quad [404]$$

The soluble ferrocyanides, as a rule, crystallise readily, and the crystals usually contain several molecules of water, thus:—

$(NH_4)_4Cfy.\ 3H_2O$, $(NH_4)_2K_2Cfy$, $(NH_4)_2K_2Cfy$.

$Na_4Cfy.12H_2O$, $Na_2K_2Cfy.6H_2O$, $Ba_2Cfy.6H_2O$.

$K_2Ba''Cfy.\ 3H_2O$, $Zn_2''Cfy.\ 3H_2O$, $(C_2H_5)_4Cfy.6H_2O$.

449. **Ferricyanides.**—By passing $Cl\text{-}Cl$ through a solution of K_4Cfy_6 a compound is formed, $K_6[Cfy_2]$, containing the bivalent radical $(Cfy\text{-}Cfy)''$, which sustains the same relation to Cfy that Tl_2 bears to $[Tl_2]''$. On evaporating the solution we obtain the salt in deep red crystals, which are an article of commerce under the name of Red Prussiate of Potash.

$$(2\,K_4Cfy_6 + Cl\text{-}Cl + Aq) = (K_6[Cfy_2] + 2\,KCl + Aq). \quad [405]$$

Other ferricyanides may be obtained from the potassium salts by metathesis.

$H_6[Cfy_2]$, $Na_6[Cfy_2].H_2O$, $Na_3K_3[Cfy_2]$, $K_3Ba_3[Cfy_2].3H_2O$.

With a solution of potassic ferricyanide ferrous salts give a deep blue precipitate called Turnbull's Blue.

$$(3\,Fe''Cl_2 + K_6[Cfy_2] + Aq) = Fe_3''[Cfy_2] + (6\,KCl + Aq). \quad [406]$$

Ferric salts, on the other hand, give no precipitate, and it will be noticed that, while these salts give a blue precipitate with the ferrocyanides, the ferrous salts give a blue precipitate only with the ferricyanides. Hence a simple means of distinguishing the two classes of salts.

450. **Other Compounds of Cyanogen.**—Chlorine forms with cyanogen two polymeric compounds.

$\underset{\text{Liquid.}}{(CN)\text{-}Cl}$ (B. P. 15.°5), $\underset{\text{Solid.}}{(C_2N_2)_n Cl_2}$.

In like manner there are two polymeric oxygen acids.

$$\underset{\text{Cyanic Acid.}}{H\text{-}O\text{-}(CN)}, \qquad \underset{\text{Cyanuric Acid.}}{H_3{}^{\equiv}O_3{}^{\equiv}(C_3N_3)}.$$

The tendency to polymerism (§ 55), here manifested, is a remarkable feature of the cyanogen compounds, and gives rise to products of great complexity, most of which, however, have been but little studied. Their condensed molecules are evidently held together by complex radicals formed by the coalescing of several atoms of cyanogen, and it is evident that the atomicity of such radicals must be equal to the number of elementary atoms of any one kind, nitrogen or carbon, of which they consist. On the same principle the constitution of the ferro- and ferri-cyanides, as well as that of paracyanogen, may be explained.

451. **Cyanates.** — Cyanic acid, referred to above, forms an important class of salts which have a great theoretical interest on account of the remarkable transformations of which many of them are susceptible. Potassic cyanate is readily prepared by dropping litharge into the fused cyanide, or ferrocyanide, so long as the oxide is reduced.

$$KCy + PbO = K\text{-}O\text{-}Cy + Pb. \qquad [409]$$

In order to crystallize the salt the fused mass should be exhausted with alcohol of 80%, since on evaporating an aqueous solution the salt is slowly decomposed. The same change takes place rapidly when the salt is heated with potassic hydrate.

$$K\text{-}O\text{-}CN + K\text{-}O\text{-}H + H_2O = K_2{}^{=}O_2{}^{=}CO + NH_3. \qquad [410]$$

When potassic cyanate is mixed in solution with ammonic sulphate, a metathesis takes place, but the resulting ammonic cyanate is at once transformed into a remarkable compound ammonia or amide (§ 418) called urea,

$$NH_4\text{-}O\text{-}CN = (H_2N)_2{}^{=}CO, \qquad [411]$$

and by this reaction the synthesis of this complex organic product was first accomplished.

452. **Sulpho-cyanates.** — By fusing potassic cyanide with sulphur we obtain the sulphur salt corresponding to potassic cyanate, or *K-S-Cy*, and from this, as from the cyanate, a large number of compounds may be derived. Potassic sulpho-cyanate, although without action on the ferrous compounds, strikes a deep red color in a solution which contains the least trace of a ferric salt, and for this reason is a very useful reagent.

CARBON AND HYDROGEN.

421. **"Organic Chemistry."** — It has already been stated that organized beings consist of materials composed, almost exclusively, of only four elements, carbon, hydrogen, oxygen, and nitrogen; nevertheless, few as are the chemical elements concerned in the processes of organic life, the number of compounds which have been discovered in the tissues of animals and plants, or formed by their chemical metamorphosis, is exceedingly great. Such compounds are called *Organic Compounds*, and in works on chemistry they are usually studied together under the separate head of *Organic Chemistry*.

While the molecules of mineral compounds consist for the most part of only a few atoms, those of organic compounds frequently contain a very large number, and the diversity in organic chemistry is obtained, not by multiplying the number of elements, but by varying the molecular grouping. It was formerly supposed that the great complexity thus produced was sustained by what was called the vital principle; but although the cause which determines the growth of organized beings is still a perfect mystery, we now know that the materials of which they consist are subject to the same laws as mineral matter, and the complexity may be traced to a peculiar quality of carbon, already described.* The atoms of carbon are prone to combine among themselves, and the same tendency which appears in several of the elements to a limited extent is developed in the case of carbon to a very high degree. Carbon is the skeleton of an organic compound in a peculiar sense. Its atoms, locked together like so many vertebræ, form the framework to which the other elements are fastened, and thus a complex molecular structure is rendered in a wonderful measure compact and stable.

Organic chemistry is simply the chemistry of the compounds of carbon, and has no distinctive character except that which the peculiar qualities of this singular element give. Moreover, although in a compendium of the science it may be convenient, or even necessary, to distinguish between mineral and organic chemistry, on account of the great preponderance and importance of the compounds of carbon, yet in a work on Chemical Philosophy, where the object is not to enumerate facts, there seems to be no good reason for departing, in the case of this

* The student should very carefully review Chap. VIII. in this connection.

single element, from the general scheme, or treating it more fully than is required to illustrate the new and important principles which it presents to our notice. Indeed, in an elementary work no other course is possible, since a mere list of the known compounds of carbon would fill this volume.

The chief differences between organic and mineral chemistry arise from the different methods of study which the present condition of these two departments of chemical science necessarily involves. Mineral substances, as a rule, present well marked and characteristic properties, by which they are distinguished from each other entirely independently of their chemical composition or relations. Galena, Feldspar, Green Vitriol, Epsom Salts, are individual substances familiar to the miner or the druggist by their physical characters, and were known under these trivial names long before men discovered of what they were composed. Their external characters alone may be objects of study, and furnish a basis for classification. So true is this, that many students of mineralogy never pass beyond this point, and know minerals only as they would any other natural objects. Moreover, when we rise to a higher level, and look upon mineral substances as chemical compounds, the most general knowledge of the composition gives us a basis for distinction. If we learn that one substance is plumbic sulphide, and another crystallized ferrous sulphate, we have gained all the knowledge which is at present necessary either to identify or to define these substances, and this kind of identification or definition is rendered the more easy by the circumstance that the compounds of each element have a certain family likeness, and that most of the elementary atoms only admit of the simpler types of combination. Indeed, until within twenty-five years, chemists generally considered that the properties and relations of a chemical compound were wholly determined by the nature of the elementary substances of which it consisted, and when, after carefully describing a substance, they had analyzed and determined its empirical symbol, they considered that they had learned all that could be known in regard to it. And although through an extension of the principles developed by the investigation of organic compounds we have gained some insight into the molecular structure of mineral products, yet this knowledge is still very imperfect, and wholly subordinate to those features of their chemical history we have just described, and this description of the method of Mineralogy not unfairly represents the present methods of "Inorganic Chemistry."

Passing now to "Organic Chemistry," we find an entire change of methods and modes of thought, although mineralogy and organic chemistry are simply different departments of one science. To the organic chemist the external characters of the bodies he studies are of secondary importance. They are for the most part colorless liquids or equally colorless solids. The chemist carefully determines their density, their boiling and melting points, perhaps also their crystalline form, and other characters, which will enable him to recognize the substances when he meets them again; for, as a rule, these compounds are so little marked that the recognition of the products of a reaction is often the great difficulty in the whole investigation. But such characters give a very small basis for association or classification, and the same is true of the composition. The ultimate analysis of organic compounds is as a rule easily made, and the empirical formula readily established. But when there may be several distinct substances consisting of the same elements united in the same proportions, a knowledge of the percentage composition can, obviously, give but little help in defining them, and it was the study of such isomeric bodies which forced the chemists to seek a new basis for distinction, and this basis they found in what we now call molecular structure (Chap. VIII.). The conception that molecular structure is a chief element in determining the properties and relations of a substance, opened a new field of investigation, which has been cultivated with the most marked success, and for several years this has been the great point of interest in connection with organic products. It so far engrosses attention that these compounds are chiefly known and defined on this basis. An aldehyde, a glycol, or a quinone is not in the mind of the chemist so much a body having certain general characters as a molecule having a certain structure. Hence the only points which we have to illustrate in connection with the compounds we are now to study is the molecular structure, and the reactions by which this structure is made evident, and the plan of this book will enable us to give only a very partial outline even of this special feature of organic chemistry.

In studying this subject the student should look for the evidence of molecular structure which the reactions as given afford, and seek to interpret these reactions from this point of view. He must constantly bear in mind, however, that our methods of representing molecular structure are purely conventional, and that our so-called structural formulæ are simply "symbols" which indicate to the chemist the re-

actions of which a given substance is susceptible. They prefigure, as it were, these reactions, and thus suggest relations which otherwise might have remained unknown. Based in the first place on a partial knowledge of the reactions of a compound, they serve to generalize that knowledge, and thus, like working theories in other sciences, they become guides to the investigator. The danger is that we should associate with them an objective reality, forgetting that the only thing they even symbolically represent are the reactions, or other relations, they are known to typify (compare § 34). For this reason the author does not attach much importance to the precise mode of writing the symbols, so long as the relations to be represented are made plain; and, in his view, essentially different formulæ are equally legitimate if both indicate all known relations.

The linear form of writing graphic symbols adopted in this book has already been explained (§ 34). It saves space and labor in printing, and in addition it appears to the author to have an advantage from the very circumstance that the student cannot draw a false impression from symbols so obviously conventional. In extending this system to the more complex carbon compounds, the common usage in works on organic chemistry may at times be violated. This will be conspicuously the case in the occasional use of *Ho* for the group *H-O-*, an abbreviation which at times greatly helps to make prominent the relations of the parts of the linear symbols, especially the relations of the hydroxyl group to the univalent atoms which it replaces. This, however, is with the author a mere question of expression. The abbreviation means the same as the full symbol, and in this, as in all other cases, the student can readily develop the condensed expression into the usual expanded graphic form.

454. **Carbon Nucleus.** — It has been shown (§ 35) that the atoms of carbon have the unique power of combining almost indefinitely with each other, and may thus give rise to nuclei around which molecules of very great complexity can be constructed, the atoms of carbon locked together, like so many vertebræ, forming the framework to which the other atoms are fastened. The molecules of the hydrocarbons, for example, are formed by uniting to the carbon skeleton atoms of hydrogen.

Obviously we may arrange the carbon atoms of the nucleus in one of two general ways: either in an open chain, Fig. *a*, or in a closed chain, Fig *b*.

Fig. a.

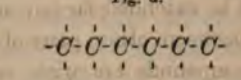
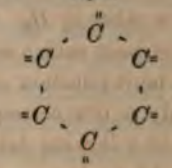


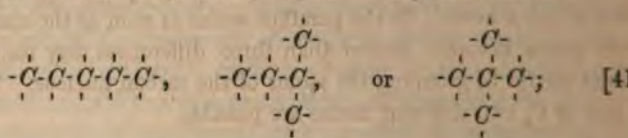
Fig. b.



These are two distinct types of structure, which determine different chemical relations. Compounds formed after the first type belong to what we may call the Fat Series, and those formed after the second type to the Aromatic Series. We will study these two types of structure separately, beginning with the open chains.

HYDROCARBONS OF THE FAT SERIES, AND THEIR DERIVATIVES. — OPEN CHAINS.

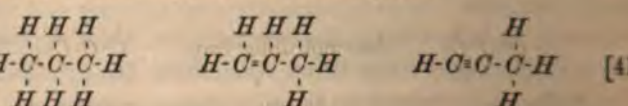
455. **Classification.** — The open chain may be either simple or forked. Thus with five atoms of carbon we may have either



[412]

and if to the open bonds we attach atoms of hydrogen, it is obvious that we shall have in each of these cases C_5H_{12}, and it can also easily be seen that with any number of carbon atoms united by *single* bonds we shall obtain a hydrocarbon conforming to the general symbol C_nH_{2n+2}, whether the chain be single or forked, provided only that it remains open. By substituting for n in this formula successive integers, we obtain the symbols of a series of hydrocarbons which differ each from the preceding by CH_2. Compounds so related are said to be *homologues*, and such a series is called an *homologous series*.

In the symbols [412] the carbon atoms are united by single bonds, and this is the smallest number of bonds by which the atoms of the nucleus can be held together. Evidently, however, a larger number of bonds may be so occupied ; as, for example, in



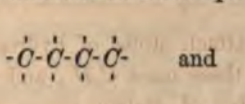
[413]

and we thus obtain a series of hydrocarbons, C_3H_8, C_3H_6, C_3H_4, which differ from each other by H_2. Compounds so related are said to be *isologues*. Theoretically such a series might be extended far beyond three terms by the multiplication of bonds between other pairs of carbon atoms, but only a few corresponding compounds are with certainty known. In the following table of hydrocarbons the vertical columns present series of homologues, and the horizontal lines series of isologues.

Hydrocarbons.

Paraffines. C_nH_{2n+2}		Olefines. C_2H_{2n}		Acetylenes. C_2H_{2n-2}	
Methane,	CH_4	Unknown,	CH_2	Unknown,	C
Ethane,	C_2H_6	Ethene,*	C_2H_4	Ethine,	C_2H_2
Propane,	C_3H_8	Propene,	C_3H_6	Propine,	C_3H_4
Butane,	C_4H_{10}	Butene,	C_4H_8	Butine,	C_4H_6
Pentane,	C_5H_{12}	Pentene,	C_5H_{10}	Pentine,	C_5H_8

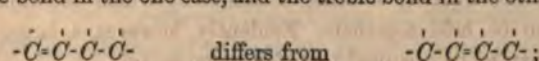
This table, however, does not by any means, represent all the possibilities of the scheme. In the paraffine series as soon as the number of carbon atoms becomes greater than three, differences may result from different modes of grouping the atoms of the carbon nucleus. Thus in the case of C_4 two different modes are possible.



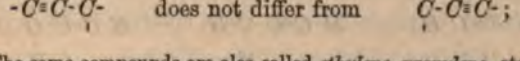
[414]

When the number of carbon atoms becomes five, three different modes are possible, as shown by [412]; and as the number of carbon atoms increases, the possible forms greatly multiply. Such differences correspond to possible isomers, not only of the hydrocarbon, but also of the compounds derived from them (compare § 33).

Isomeric modifications of the olefines and acetylenes may arise, not only from the differences just described, but also from the position of the double bond in the one case, and the treble bond in the other. Thus,



but



* The same compounds are also called *ethylene, propylene*, etc.

and the student must carefully bear in mind that our symbols are merely conventional modes of representing molecular structure, and that only those differences of form in the symbols have significance which indicate a difference in the relative position of the parts entirely independent of the manner in which this may be represented on the page. Indeed, there is a great difference of practice in regard to the manner of writing and printing structural symbols of this kind.

456. **Paraffines.** — Each of the three series of hydrocarbons, classified above, is marked by certain characteristic chemical relations. The paraffines are highly indifferent bodies, and this property corresponds to the fact that they are saturated compounds. As the atoms are all joined by single bonds, no products can be formed from these bodies except by substitution or by the breaking up of the molecules. The first member of this series is the well-known "Marsh Gas," a constant product of the decomposition of vegetable tissue under water, also the chief constituent of the fire-damp of coal mines, and of common illuminating-gas obtained by the dry distillation of coal. Several of the successive homologues of marsh gas may be prepared by various reactions, and the higher members of the series are constituents of the petroleums of commerce, from which they can be more or less perfectly separated by fractional distillation.

457. **Olefines.** — The olefines are not saturated compounds, but are capable of fixing two additional univalent atoms, and of acting as bivalent radicals. The first member of the series was discovered by an association of Dutch chemists in 1795, who, noticing its characteristic property of combining directly with chlorine, called it Olefiant (oil-making) Gas, because the product of this union is a thick-flowing liquid. This product, long known as the Oil of the Dutch chemists, is ethylene chloride, $C_2H_4Cl_2$. Ethylene bromide and ethylene iodide may be formed in a similar way, and the tendency to form compounds of this type distinguishes this class of hydrocarbons, which are called, for this reason, *Olefines*. Moreover, the hydrogen atoms of the bivalent radical may all be replaced by chlorine or bromine, and the resulting compound still retain the same typical character.

Olefiant gas is most readily obtained by heating alcohol with several times its volume of strong sulphuric acid. The reaction is somewhat complicated, but the result is a dehydration of the alcohol, and the same effect may be produced with zincic chloride (§ 232).

$$C_2H_6O - H_2O = C_2H_4. \qquad [415]$$

Olefiant gas combines directly, not only with chlorine, bromine, etc., but also with the hydrogen acids.

$$C_2H_4 + HI = C_2H_5I. \qquad [416]$$

Moreover, it unites with hypochlorous acid, forming a chlorhydrine.

$$C_2H_4 + H\text{-}O\text{-}Cl = (C_2H_4)^{\prime\prime}HO,Cl. \qquad [417]$$

Containing twice as much carbon in the same volume, olefiant gas burns with a more luminous flame than marsh gas, and the illuminating power of coal gas is due in no inconsiderable measure to its presence. Several of the other members of this series of hydrocarbons are also found in the products of the dry distillation of coal.

458. **Acetylenes.** — The molecules of the acetylenes fall short of saturation by four univalent atoms, and are therefore quadrivalent. Ethine, better known as acetylene, the first member of the series, is a constant product of the incomplete combustion of all forms of hydrocarbon fuel, and can be obtained abundantly by drawing the products of combustion of a Bunsen lamp, burning at the base, through a solution of $AgCl$ in aqua ammonia. By this solution the acetylene is absorbed, and the compound $C_2H_2Ag_2O$ separates out in the form of a white precipitate. When the washed and still moist precipitate is next boiled with hydrochloric acid, acetylene gas is evolved, and chloride of silver reproduced, which if redissolved in ammonia may be used over and over for the same purpose. A similar compound, $C_2H_2[Cu_2]O$, is formed by passing the products of incomplete combustion through an ammoniacal solution of Cu_2Cl_2. This cuprous compound has a blood-red color, and serves as a very delicate test of the presence of acetylene; and the formation of compounds of this type is a very characteristic feature of this series of hydrocarbons, which contain the group $-C{\equiv}C-$.

Acetylene acts as a bivalent as well as a quadrivalent radical. When exposed to nascent hydrogen, each molecule takes up H_2, and it changes to olefiant gas (C_2H_4). It unites directly with bromine to form first $C_2H_2Br_2$, and afterwards $C_2H_2Br_4$. It unites also with HBr to form either C_2H_3Br or $C_2H_4Br_2$. These reactions can be easily reversed; and since ethylene bromide is easily prepared from olefiant gas, it affords, when boiled with an alcoholic solution of potash, an excellent source of acetylene.

$$C_2H_4Br_2 + 2KOH = 2KBr + 2H_2O + C_2H_2 \qquad [418]$$

459. **Methods of Synthesis.** — In all departments of the science, and especially in organic chemistry, the processes by which the more complex and less stable products are formed from those which are simpler in structure and more permanent, have a peculiar interest. As has been already shown (§ 70), there is in every chemical change a tendency to those products whose formation will determine the evolution of the greatest amount of heat, and we can reverse this tendency only by an expenditure of energy. On the surface of the earth the radiant energy of the sun is constantly doing work of this sort, and determining the formation of those complex products which are the results of organic life. Such products represent a large amount of latent energy, and tend to fall back into a more stable state when the energy reappears as heat. Of course the mode of action by which matter is thus raised to a higher plane is a subject of the greatest interest, and this interest attaches to the synthetical methods of organic chemistry which imitate the processes of nature. With these methods recent investigators have had wonderful success, and the artificial production of such substances as alizarine and indigotine must be regarded as among the greatest achievements of modern science. The student will appreciate the wonderful character of these results if he reflects that to build up a complex molecular structure in opposition to the atomic forces is the equivalent in architecture of supporting a roof of vaulted masonry in opposition to the force of gravitation, and implies a similar skill.

Again, the chemist finds great interest in synthetical processes, because they furnish such direct indications of molecular structure. As we thus proceed link by link to construct complex products from simple binary compounds, we are able to rivet together a chain of evidence which establishes the molecular structure of these compounds with a very high degree of certainty.

For these reasons we shall give a large number of synthetical reactions in the following pages; and in this section we give the reactions by which the synthesis of the hydrocarbons has been effected, starting from elementary substances or simple compounds of the elements. The student should seek to trace the chain of reasoning from the first. We obtain [419] by passing the two aeriform factors over ignited copper, and [420] when a powerful electric current passes between carbon poles in an atmosphere of hydrogen.

$$CS_2 + 2\,H_2S + 4\,Cu = 4\,CuS + CH_4. \qquad [419]$$

$$C_2 + H_2 = C_2H_2. \qquad [420]$$

$$\underset{\text{By nascent hydrogen.}}{C_2H_2} + H_2 = C_2H_4. \qquad [421]$$

$$\underset{\text{By direct union.}}{C_2H_4} + HBr = C_2H_5Br. \qquad [422]$$

$$\underset{\text{By nascent hydrogen.}}{C_2H_5Br} + H_2 = C_2H_6 + HBr. \qquad [423]$$

$$CH_3I^* + Na_2 + CH_3I = CH_3\text{-}CH_3 + 2\,NaI. \qquad [424]$$

$$2\,C_2H_5I + (CH_3)_2Zn = 2\,C_2H_5\text{-}CH_3 + ZnI_2. \qquad [425]$$

The last two reactions enable us to form from lower homologues paraffines of a higher order, and then we can convert a paraffine into an olefine thus: —

$$C_3H_7I + KOH = KI + H_2O + C_3H_6.\dagger \qquad [426]$$

Lastly, having combined the olefine with Br_2, we can convert it into an acetylene by [418].

DERIVATIVES FROM THE HYDROCARBONS. — WITH OPEN CHAINS.

460. **Addition Products**, formed only from unsaturated hydrocarbons, like the olefines or the acetylenes. One molecule of the hydrocarbon always unites with two atoms or four atoms of the radical added; never with one atom. It is especially the atoms of the chlorine group of elements, or their hydrogen acids, which may be thus added.

$$\underset{\text{Ethylene.}}{H_2C\text{=}CH_2} + Br_2 = \underset{\text{Ethylene Bromide.}}{BrH_2C\text{-}CH_2Br}. \qquad [427]$$

$$\underset{\text{Ethylene.}}{H_2C\text{=}CH_2} + HBr = \underset{\text{Ethylic Bromide.}}{H_3C\text{-}CH_2Br}. \qquad [428]$$

But other compounds may also be taken.

$$H_2C\text{=}CH_2 + HOCl = \underset{\text{Ethylene Chlorhydrine.}}{Ho.H_2C\text{-}CH_2Cl}. \qquad [429]$$

Compounds thus resulting are identical with the corresponding compounds formed by substitution, as shown in the next section.

461. **Substitution Products.** The hydrogen atoms of the hydrocarbons may be replaced by various radicals, both simple and compound, and, even when not thus actually formed, we can best classify the great variety of organic products on the basis of this assumed derivation.

* For the formation CH_3I, etc., see [430], beyond.

† CH_3I, under the same conditions, gives methyl alcohol, $CH_3\text{-}O\text{-}H$.

Substitution of Chlorine, Bromine, etc.

Substitution may be effected by the direct action of chlorine, bromine, or iodine (compare § 30).

$$\underset{\text{Ethane.}}{C_2H_6} + Cl_2 = \underset{\text{Ethylic Chloride.}}{C_2H_5Cl} + HCl. \qquad [430]$$

We thus obtain compounds of the haloids with the radicals methyl, ethyl, etc., already described (§ 35). Such compounds, however, are usually made by the action of the haloid acids on the alcohols.

$$\underset{\text{Ethylic Alcohol.}}{C_2H_5OH} + HBr = C_2H_5Br + H_2O.$$

The univalent radicals just referred to are frequently called *alkyl* radicals, and those which contain more than two atoms of carbon may have isomeric forms; the differences between which depend, not only on the grouping of the atoms of the carbon nucleus, but also on the position of the open bond. Thus: —

Methyl, CH_3 No isomers.

Ethyl, C_2H_5 No isomers.

Propyl, C_3H_7 Two isomers, —

$$CH_3\text{-}CH_2\text{-}CH_2\text{-} \qquad CH_3\text{-}\dot{C}H\text{-}CH_3 \qquad [431]$$

Butyl, C_4H_9 Four isomers, —

$$\underset{\text{Normal Form.}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}} \qquad \underset{\text{Secondary Form.}}{CH_3\text{-}CH_2\text{-}\dot{C}H\text{-}CH_3} \qquad [432]$$

$$\underset{\text{Iso Form.}}{CH_3, CH_3\text{-}CH\text{-}CH_2\text{-}} \qquad \underset{\text{Tertiary Form.}}{CH_3, CH_3\text{-}\dot{C}\text{-}CH_3}$$

These names are important, and will reappear in the various compounds of these radicals. By adding an atom of chlorine at the open bond, we obtain in each case the symbols of the chlorides of the several isomeric forms. In these compounds one only of the hydrogen atoms of the hydrocarbon molecule has been replaced; but by continuing the action of the halogen, the remaining atoms may be replaced either wholly or in part, and the possibilities of isomerism in the resulting products become an interesting subject of study. Thus, when two atoms of hydrogen have been replaced by chlorine, we have

$C_2H_2Cl_2$ No isomers.

CH_4Cl_2 Two isomers, —

$$\underset{\text{Ethylidene Chloride.}}{CH_3\text{-}CHCl_2} \qquad \underset{\text{Ethylene Chloride.}}{CH_2Cl\text{-}CH_2Cl} \qquad [433]$$

$C_3H_6Cl_2$ Four isomers, —

$$CH_3\text{-}CH_2\text{-}CHCl_2 \qquad CH_3\text{-}CHCl\text{-}CH_2Cl$$
$$CH_3\text{-}CCl_2\text{-}CH_3 \qquad CH_2Cl\text{-}CH_2\text{-}CH_2Cl \qquad [434]$$

Substitution of Oxygen Radicals.

Replacing one atom of hydrogen by *Ho*, we obtain *Alcohols*. Thus,

$$C_2H_6 \text{ gives } \underset{\text{Ethylic Alcohol.}}{C_2H_5\text{-}Ho}.$$

Replacing by *Ho* two of the atoms of hydrogen, which are not united to the same carbon atom, we obtain *Glycols*. Thus,

$$CH_3\text{-}CH_3 \text{ gives } \underset{\text{Ethylic Glycol.}}{Ho\,CH_2\text{-}Ho\,CH_2} \qquad [435]$$

If three atoms of hydrogen, united to three distinct carbon atoms, are each replaced by *Ho*, we obtain *glycerines*. Thus,

$$CH_3\text{-}CH_2\text{-}CH_3 \text{ gives } Ho\,CH_2\text{-}Ho\,CH\text{-}Ho\,CH_2 \qquad [436]$$

Compounds with Ho_4, Ho_5, and Ho_6, in place of a corresponding number of hydrogen atoms, have been recognized.

If we replace two hydrogen atoms united to the same carbon atom by *Ho*, the contiguous hydroxyl groups react on each other. A molecule of water is formed, and the result is a substitution in the hydrocarbon of oxygen. If this substitution takes place at the end of the chain, the product is an *Aldehyde;* if in the middle of the chain, the product is a *Ketone*.

$$CH_3\text{-}CH_3 \text{ gives } CH_3\text{-}CH,Ho_2 = \underset{\text{Aldehyde.}}{CH_3\text{-}CO,H} + H_2O \qquad [437]$$

$$CH_3\text{-}CH_2\text{-}CH_3 \text{ gives } CH_3\text{-}CHo_2\text{-}CH_3 = \underset{\text{Ketone.}}{CH_3\text{-}CO\text{-}CH_3} + H_2O \qquad [438]$$

If we replace three hydrogen atoms united to the same carbon atoms by *Ho*, a similar action results, and an acid is formed as

$$CH_3\text{-}C^2Ho_3 = H_2O + CH_3\text{-}CO\text{-}Ho = H_2O + CH_3\text{-}CO\text{-}O\text{-}H.$$

1st Stage, $CH_3\text{-}CH_2\text{-}O\text{-}H + O = CH_3\text{-}CO\text{-}H + H_2O.$ [444]

2d Stage, $CH_3\text{-}COH + O = CH_3\text{-}CO\text{-}O\text{-}H.$ [445]

464. **Secondary Alcohols.** — These are not possible with less than three atoms of carbon in the molecule. Examples are

$$\underset{\text{Isopropyl Alcohol.}}{(CH_3)_2\text{=}CH\text{-}O\text{-}H} \qquad \underset{\text{Secondary Butyl Alcohol.}}{CH_3,C_2H_5\text{=}CH\text{-}O\text{-}H} \qquad [446]$$

They can be made from corresponding iodides or sulphates by the same reactions as primary alcohols [439, 440, 442, and 443]. They can also be prepared from ketones by the action of nascent hydrogen.

$$\underset{\text{Ketone.}}{(CH_3)_2\text{=}CO} + H_2 = \underset{\text{Isopropyl Alcohol.}}{(CH_3)_2\text{=}CH\text{-}O\text{-}H} \qquad [447]$$

As the primary alcohols give aldehydes, so the secondary alcohols give ketones, as the first stage of their oxidation.

$$(CH_3)_2\text{=}CH\text{-}O\text{-}H + O = \underset{\text{Ketone.}}{(CH_3)_2\text{=}CO} + H_2O. \qquad [448]$$

When further oxidized the ketone splits up and yields one or more products whose molecules contain a less number of carbon atoms.

$$\underset{\text{Ketone.}}{(CH_3)_2\text{=}CO} + 3O = \underset{\text{Acetic Acid.}}{CH_3\text{-}CO\text{-}O\text{-}H} + \underset{\text{Formic Acid.}}{H\text{-}CO\text{-}O\text{-}H} \qquad [449]$$

465. **Tertiary Alcohols.** — These are not possible with less than four carbon atoms in the molecule. For example, —

$(CH_3)_3\text{=}C\text{-}O\text{-}H$, Tertiary Butyl Alcohol. [450]

They may be prepared from the corresponding iodides or sulphates by reactions [439, 440, 442, and 443]. When oxidized they split up at once into acids with a less number of carbon atoms in the molecule. Hence the three classes of alcohols are distinguished by the products they yield when oxidized. The following characteristics, however, are common to all the alcohols. When acted on by the haloid acid, *Ho* is replaced by *Cl*, *Br*, or *I*.

$$\underset{\text{Methyl Alcohol.}}{CH_3\text{-}Ho} + HBr = \underset{\text{Methyl Bromide.}}{CH_3Br} + H_2O \qquad [451]$$

When *HI* is used in excess, *Ho* is replaced by *H*.

$$CH_3\text{-}Ho + 2\,HI = CH_3\text{-}I + HI + H_2O = CH_4 + H_2O + I_2. \qquad [452]$$

The H in $R\text{-}O\text{-}H$ may be replaced by acid radicals, as in

$$\underset{\text{Ethylic Nitrate.}}{C_2H_5\text{-}O\text{-}NO_2} \qquad \underset{\text{Ethylic Acetate.}}{C_2H_5\text{-}O\text{-}C_2H_3O} \qquad [453]$$

The H in $R\text{-}O\text{-}H$ may also be replaced by hydrocarbon radicals, either the same as that with which the hydroxyl is combined, or a different one; as in

$$\underset{\text{Ethylic Ether.}}{C_2H_5\text{-}O\text{-}C_2H_5} \qquad \underset{\text{Methyl Ethylic Ether.}}{C_2H_5\text{-}O\text{-}CH_3} \qquad [454]$$

The H in $R\text{-}O\text{-}H$ may be replaced by an alkaline metal.

$$2\ \underset{\text{Ethylic Alcohol.}}{C_2H_5\text{-}O\text{-}H} + K_2 = 2\ \underset{\text{Potassic Ethylate.}}{C_2H_5\text{-}O\text{-}K} + H_2 \qquad [455]$$

It thus appears that the alcohols act both as acid hydrates towards the alkaline metals, and as basic hydrates towards the acid radicals. In both relations they manifest a weak polarity, and their more characteristic feature is that of a weak base. The relations of the alcohols and ethers to metallic hydrates and oxides have already been fully discussed (§ 41).

466. **Nomenclature.** — The numerous complex modifications of structure which have been observed among the alcohols has led to the general adoption of a peculiar nomenclature capable of designating the different varieties. The group $\equiv C\text{-}O\text{-}H$, characteristic of all alcohols, has been called carbinol, and the various alcohols are called different kinds of carbinol according to the nature of the radicals added to the group to complete the molecule, not designating, however, the single atoms of hydrogen. Thus trimethyl carbinol $(CH_3)_3\equiv C\text{-}O\text{-}H$ is a tertiary alcohol; ethyl methyl carbinol, $CH_3, C_2H_5, H\equiv C\text{-}O\text{-}H$, is a secondary alcohol; and isobutyl carbinol, a primary alcohol, may be written $R, H_2\equiv C\text{-}O\text{-}H$, in which R stands for isobutyl having the structure given on page 562.

467. **Unsaturated Alcohols.** — Alcohols may be formed by substituting Ho for H in the molecules of the unsaturated hydrocarbons (§§ 457 and 458), and the product has the relations both of an alcohol and of an unsaturated molecule. A good example is

$$(CH_2\text{=}CH)\text{-}CH_2\text{-}O\text{-}H, \text{ Allyl Alcohol.}$$

468. **Glycols and Glycerines** illustrate the same principles as the alcohols, which they resemble in their relations, only these are more complex. The glycols contain Ho_2, and are diatomic compounds. The glycerines contain Ho_3, and are triatomic compounds (§ 43).

469. **Aldehydes** can theoretically be made by replacing H_2 on the same carbon atom of a hydrocarbon by O [437]. Practically they are prepared by the oxidation of the primary alcohols [444], and form an intermediate stage between the alcohol and the corresponding fat acid. Acetic aldehyde, the best known and most important of these bodies, can be made by heating together a mixture of calcic acetate and calcic formiate.

$$\underset{\text{Calcic Acetate.}}{Ca{=}O_2{=}(CO{\cdot}CH_3)_2} + \underset{\text{Calcic Formate.}}{Ca{=}O_2{=}(CO{\cdot}H)_2} = 2\,Ca{=}O_2{=}CO + 2\,\underset{\text{Aldehyde.}}{CH_3{\cdot}COH}. \quad [456]$$

By a similar reaction other aldehydes may be formed. The aldehydes are reducing agents. Compare [445].

$$CH_3{\cdot}COH + Ag_2O = CH_3{\cdot}CO{\cdot}O{\cdot}H + Ag_2. \quad [457]$$

By nascent hydrogen they are changed to alcohols [441]. The O of an aldehyde molecule can be replaced by Cl_2 as in ethylidene chloride, $CH_3{\cdot}CCl_2H$. The aldehydes tend to "polymerize," as in $C_3H_6O_3$, which is obviously a polymeric form of formyl aldehyde, CH_2O. They also form characteristic addition products.

$$\underset{\text{Aldehyde.}}{CH_3{\cdot}C{=}O,H} + NH_3 = \underset{\text{Aldehyde Ammonia.}}{CH_3{\cdot}C{=}H,Ho,NH_2}. \quad [458]$$

$$CH_3{\cdot}COH + HCN = CH_3{\cdot}CH{=}Ho,CN. \quad [459]$$

$$CH_3{\cdot}COH + H,Na{=}O_2{=}SO = (CH_3{\cdot}CHHo),Na{=}O_2{=}SO. \quad [460]$$

Further examples of addition products are

$$\underset{\text{Acetal.}}{CH_3{\cdot}CH(O{\cdot}C_2H_5)_2}, \quad \text{and} \quad \underset{\text{Aldehyde Acetate.}}{CH_3{\cdot}CH(O{\cdot}C_2H_3O)_2}. \quad [461]$$

Of the substitution products of the aldehydes the most important is chloral, $CCl_3{\cdot}C{=}O,H$, from which by the addition of water is derived chloral hydrate, $CCl_3{\cdot}CH,Ho_2$.

470. **Ketones.** — The relation of these bodies to the secondary alcohols has already been stated (§ 464). The most important of the ketones is acetone $(CH_3)_2{=}CO$, and the presence of the radical $=CO$ connected by both its bonds with alkyl radicals is the most characteristic feature of their molecular structure. Acetone may be prepared by the dry distillation of calcic acetate.

$$Ca{=}O_2{=}(CO{\cdot}CH_3)_2 = Ca{=}O_2{=}CO + \underset{\text{Acetone.}}{(CH_3)_2{=}CO}. \quad [462]$$

Also by the action of zinc methyl on acetyl chloride.

$$2\,CH_3\text{-}CO\text{-}Cl + Zn(CH_3)_2 = ZnCl_2 + 2\,CH_3\text{-}CO\text{-}CH_3. \quad [463]$$

The relation of the ketones to the aldehydes may thus be shown :—

$$\underset{\text{Acetic Aldehyde.}}{CH_3\text{-}CO\text{-}H} \qquad \underset{\text{Acetone.}}{CH_3\text{-}CO\text{-}CH_3} \quad [464]$$

When on oxidation a ketone molecule breaks up, the carbon atoms are divided between the two acid molecules thus formed as evenly as possible.

$CH_3\text{-}CO\text{-}C_2H_5$ gives $2\,CH_3\text{-}CO\text{-}O\text{-}H$.

$CH_3\text{-}CO\text{-}C_3H_7$ gives $CH_3\text{-}CO\text{-}O\text{-}H$ and $C_2H_5\,CO\text{-}O\text{-}H$.

By partial reduction ketones give secondary glycols called Pinakones, two molecules of the ketone coalescing to form the molecule of the pinakone.

$$\underset{\text{Ketone.}}{2(CH_3)_2\text{=}CO} + H_2 = \underset{\text{Pinakone.}}{(CH_3)_2\text{=}CHO\text{-}CHO\text{=}(CH_3)_2}. \quad [465]$$

Withdraw from the pinakones a molecule of water, and we obtain another class of compounds called Pinakolines, which are simply ketones of a higher order.

$$\underset{\text{Pinakone.}}{(CH_3)_2\text{=}CHO\text{-}CHO\text{=}(CH_3)_2} = \underset{\text{Pinakoline.}}{(CH_3)_3\text{=}C\text{-}CO\text{-}CH_3} + H_2O. \quad [466]$$

Acids.

471. **General Relations.** — The chief feature in the structure of an acid molecule is the group $-CO\text{-}O\text{-}H$ (carboxyl), and, as has been shown, the basicity of the acid depends on the number of these groups present (§§ 44 and 442). Acids may be formed by the oxidation of an alcohol, an aldehyde, or a ketone, as already shown. They may also be produced by the action of an acid or an alkali on a nitrile (§ 321).

$$\underset{\text{Acetonitrile.}}{CH_3\text{-}CN} + 2\,H_2O = CH_3\text{-}CO\text{-}Ho + NH_3. \quad [467]$$

By the action of PCl_5 (§ 341) the Ho in carboxyl can be replaced by chlorine.

$$\underset{\text{Acetic Acid.}}{CH_3\text{-}CO\text{-}Ho} + PCl_5 = \underset{\text{Acetyl Chloride.}}{CH_3\text{-}CO\text{-}Cl} + POCl_3 + HCl. \quad [468]$$

Water changes the chloride back to the acid.

$$CH_3\text{-}CO\text{-}Cl + H\text{-}O\text{-}H = CH_3\text{-}CO\text{-}O\text{-}H + HCl. \quad [469]$$

The *Ho* of carboxyl may also be replaced by NH_2 (§ 319).

$$CH_3\text{-}CO\text{-}Cl + NH_2 = \underset{\text{Acetamide.}}{CH_3\text{-}CO\text{-}NH_2} + HCl.$$

The *H* of carboxyl is very readily replaced by metallic radicals, and thus result the salts whose ready production is the chief characteristic of an acid.

$$H\text{-}O\text{-}(CO\text{-}CH_3) + Na\text{-}O\text{-}H = \underset{\text{Sodic Acetate.}}{Na\text{-}O\text{-}(CO\text{-}CH_3)} + H\text{-}O\text{-}H. \quad [470]$$

The *H* of carboxyl may also be replaced by alkyl radicals, and thus result compound ethers [453].

$$\underset{\text{Sodic Acetate.}}{Na\text{-}O\text{-}(CO\text{-}CH_3)} + \underset{\text{Ethylic Chloride.}}{C_2H_5Cl} = \underset{\text{Ethylic Acetate.}}{C_2H_5\text{-}O\text{-}(CO\text{-}CH_3)} + NaCl. \quad [471]$$

$$Cl\text{-}CO\text{-}CH_3 + C_2H_5\text{-}O\text{-}H = C_2H_5\text{-}O\text{-}(CO\text{-}CH_3) + HCl. \quad [472]$$

The *H* of carboxyl may be replaced by an acid radical, and thus result acid anhydrides (§ 42).

$$Na\text{-}O\text{-}(CO\text{-}CH_3) + (CH_3\text{-}CO)\text{-}Cl = (CH_3\text{-}CO)_2\text{=}O + NaCl. \quad [473]$$

Lastly, the hydrogen atoms of the hydrocarbon radical may be replaced as in the chloracetic acids described in § 30.

Classes of Acids.

472. **Monobasic Acids** contain one carboxyl group. The most important family is that of the fat acids, which makes a long series corresponding to the primary alcohols (§ 41), and are capable of the same isomerism as the alcohols. The formation of the fat acids by the oxidation of the corresponding alcohol is illustrated by [444 and 445]. They may also be formed from the cyanides of the alcohol radicals, and the method is interesting as indicating their molecular structure.

$$HCN + HCl + 2\,H_2O = NH_4Cl + \underset{\text{Formic Acid.}}{H\text{-}CO\text{-}Ho}. \quad [474]$$

$$C_2H_5CN + HCl + 2\,H_2O = NH_4Cl + \underset{\text{Propionic Acid.}}{C_2H_5\text{-}CO\text{-}Ho}. \quad [475]$$

The acid may be converted into the corresponding alcohol thus:—

$$\underset{\text{Potassic Acetate.}}{(CH_3\text{-}CO)\text{-}O\text{-}K} + \underset{\text{Potassic Formate.}}{(H\text{-}CO)\text{-}O\text{-}K} = \underset{\text{Aldehyde.}}{CH_3\text{-}CO\text{-}H} + K_2{=}O_2{=}CO. \quad [476]$$

$$CH_3\text{-}CO\text{-}H + H_2 = \underset{\text{Alcohol.}}{C_2H_5\text{-}O\text{-}H}. \quad [477]$$

The potassic salt of the acid is first distilled with potassic formate, and the aldehyde thus obtained transformed into alcohol with nascent hydrogen. Starting now with ethylic alcohol, we can convert it into ethylic cyanide thus:—

$$C_2H_5\text{-}O\text{-}H + H_2{=}O_2{=}SO_2 = H,C_2H_5{=}O_2{=}SO_2 + H_2O. \quad [478]$$

$$K,C_2H_5{=}O_2{=}SO_2 + K\text{-}CN = K_2{=}O_2{=}SO_2 + C_2H_5\text{-}CN. \quad [479]$$

and then by [475] we can produce propionic acid. From propionic acid, by [476 and 477], we can obtain propylic alcohol. Thus we are able to pass from one fat acid to the next, and from one alcohol to the next; and since formic acid can be made directly from its elements [381], the synthesis of this whole class of organic compounds is theoretically possible.

Our general theory that the molecules of the monobasic acids consist of carboxyl united to the alkyl radicals, is confirmed by the fact that sodic acetate may be formed by the direct union of CO_2 with sodic methide.

$$(CH_3)\text{-}Na + CO_2 = CH_3\text{-}CO\text{-}O\text{-}Na. \quad [480]$$

When the hydrocarbon radical of an acid is an unsaturated hydrocarbon, the acid has the relations of an unsaturated compound, besides the relations of an acid. Acrylic acid, $C_3H_4O_2$, is a monobasic acid of this class. Under the influence of nascent hydrogen, acrylic acid changes into propionic acid, and when acted on by bromine it yields a simple derivative of the same compound.

$$\underset{\text{Acrylic Acid.}}{H\text{-}O\text{-}(CO\text{-}CH{=}CH_2)} + H\text{-}H = \underset{\text{Propionic Acid.}}{H\text{-}O\text{-}(CO\text{-}C_2H_5)}.$$
$$H\text{-}O\text{-}(CO\text{-}CH{=}CH_2) + Br\text{-}Br = H\text{-}O\text{-}(CO\text{-}C_2H_3Br_2). \quad [481]$$

Acrylic acid is the first of an homologous series, the members of which sustain similar relations, but only a few of them have been investigated.

473. **Dibasic Acids** contain two carboxyl groups, but in the molecule of carbonic acid, $H\text{-}O\text{-}CO\text{-}O\text{-}H$, which is the simplest of these

compounds, one atom of carbonyl (CO) is divided between two Ho groups, and the polarizing power of this radical is as it were also divided. The relations of carbonic acid have already been studied (§ 440). Its amide, $CO{=}(NH_2)_2$, is the important animal secretion Urea or Carbamide, and the half-amide or amide acid $H\text{-}O\text{-}CO\text{-}NH_2$, called Carbamic acid, forms ethers called Urethanes, for example, $C_2H_5\text{-}O\text{-}CO\text{-}NH_2$. The relations of these compounds have already been described (§ 319).

In oxalic acid, which has also been described (§ 442), we find the relations of a dibasic acid fully developed. The molecules of this acid may be regarded as formed by the union of two carboxyl groups, and this is the first of a series of homologues whose relation to each other and to the monobasic acid is exhibited by the following table: —

$H\text{-}O\text{-}(CO\text{-}CO)\text{-}O\text{-}H$ (Oxalic Acid.)	$H\text{-}O\text{-}(CO\text{-}H)$ (Formic Acid.)
$H\text{-}O\text{-}(CO\text{-}CH_2\text{-}CO)\text{-}O\text{-}H$ (Malonic Acid.)	$H\text{-}O\text{-}(CO\text{-}CH_3)$ (Acetic Acid.) [482]
$H\text{-}O\text{-}(CO\text{-}C_2H_4\text{-}CO)\text{-}O\text{-}H$ (Succinic Acid.)	$H\text{-}O\text{-}(CO\text{-}C_2H_5)$ (Propionic Acid.)

In these compounds isomerism may result either from difference of structure in the hydrocarbons, or from the position of the carboxyl groups. Thus we may have

$$(H\text{-}O\text{-}CO)\text{-}CH_2\text{-}CH_2\text{-}(CO\text{-}O\text{-}H) \quad \text{(Succinic Acid.)} \qquad CH_3\text{-}CH(CO\text{-}O\text{-}H)_2 \quad \text{(Isosuccinic Acid.)} \quad [483]$$

The anhydride of succinic acid has the symbol $C_2H_4{=}(CO)_2{=}O$.

There are two remarkable isomeric groups of *unsaturated* dibasic acids formed of unsaturated hydrocarbon radicals, like the unsaturated monobasic acids above; and the study of these isomeric bodies has a special interest, because they appear to indicate that the atoms of carbon may be at times bivalent. The first group consists of two bodies, Fumaric and Maleic acids, both of which have the empirical symbol $C_4H_4O_4$, and the second group of three bodies, Itaconic, Citraconic, and Mesaconic acids, all of which have the empirical symbol $C_5H_6O_4$, and are therefore the homologues of the first.

The molecular structure usually assigned to these compounds of the first group is shown by the symbols

$$H\text{-}O\text{-}CO\text{-}CH{=}CH\text{-}CO\text{-}O\text{-}H \quad \text{(Fumaric Acid.)} \qquad H\text{-}O\text{-}CO\text{-}CH_2\text{-}C{=}CO\text{-}O\text{-}H \quad \text{(Maleic Acid.)} \quad [484]$$

The choice of symbols for fumaric and maleic acids is limited by the fact that when acted on by nascent hydrogen they both give succinic acid. Furthermore, both acids combine directly with two atoms of bromine, and though the intermediate products of this union are different, yet both bromo- and isobromo-succinic acids yield the same succinic acid when the bromine is replaced by hydrogen. The second general symbol is capable of no less than eleven variations, and the structure of the three known acids cannot with certainty be determined in all its details; but it seems to involve the same feature in that one of the carbon atoms of the nucleus is bivalent.

Malic acid, which is the acid principle of some fruits, differs from Maleic acid only by one molecule of water.

474. **Tribasic Acid.** — By removing one molecule of water from citric acid, the well-known acid principle of the lemon, we obtain Aconitic acid, which is an unsaturated tribasic acid, and has $(H\text{-}O\text{-}CO)_3$.

$$\underset{\text{Citric Acid.}}{C_6H_8O_7} - H_2O = \underset{\text{Aconitic Acid.}}{(H\text{-}O\text{-}CO)_3{=}C_3H_3}. \qquad [485]$$

475. **Alcohol Acids.** — It has already been shown that, while the atomicity of an organic acid depends on the number of hydroxyl groups, the basicity depends on the number of carboxyl groups, so that the first may be greater than the last. Acids whose atomicity is thus greater than the basicity may be called alcoholic acids, and the two classes of replaceable hydrogen atoms are distinguished as basic and alcoholic hydrogen (compare § 44).

The following classes of alcohol acids may be noticed: —

1st. Diatomic and Monobasic. To this class belongs glycolic acid, $H\text{-}O\text{-}CO\text{-}CH_2\text{-}O\text{-}H$, which is a product of the oxidation of glycol. Homologous with glycolic acid is the well-known lactic acid, which has two isomeric conditions (compare § 42).

$$\underset{\text{Paralactic Acid.}}{H\text{-}O\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}H} \qquad \underset{\text{Lactic Acid.}}{H\text{-}O\text{-}CO\text{-}H_0CH\text{-}CH_3} \qquad [486]$$

Lactic acid prepared from milk has the second form, and still a third condition of this acid is known, having apparently the same structure as the last, but differing in physical properties (physical isomerism). Acids of this class may form many anhydrides, either by the union of two molecules, or by the replacement of the two hydroxyl groups of one molecule by an atom of oxygen, which thus forms an additional link between two parts of this molecule. Thus,

$$\underset{\text{Lactic Acid.}}{H\text{-}O\text{-}CO\text{-}H_2C\text{-}CH\text{-}CH_3} - H_2O = \underset{\text{Lactone.}}{OC\text{-}CH\text{-}CH_3} \quad [486]$$

2d. Triatomic and Dibasic. Examples of such are

Tartronic Acid,	$H\text{-}O\text{-}CO\text{-}H_2C\text{-}CH\text{-}CO\text{-}O\text{-}H$	[487]
Malic Acid,	$H\text{-}O\text{-}CO\text{-}H_2C\text{-}CH\text{-}CH_2\text{-}CO\text{-}O\text{-}H$	

3d. Tetratomic and Dibasic. The best known example is

Tartaric Acid, $H\text{-}O\text{-}CO\text{-}H_2C\text{-}H_2C\text{-}CH\text{-}CO\text{-}O\text{-}H$ [489]

The remarkable physical isomerism of this substance has already been described (§ 116), and in § 44 we have given the symbols of the salts of tartaric acid which best illustrate the relations of its basicity to its atomicity.

4th. Tetratomic and Tribasic. Here belongs

Citric Acid, $H\text{-}O\text{-}CO\text{-}CH_2\text{-}(H\text{-}O\text{-}C\text{-}CO\text{-}O\text{-}H)\text{-}CO\text{-}O\text{-}H$ [490]

476. **Aldehyde and Ketone Acids.** — These exhibit a peculiar type of structure, in which atoms of hydrogen or of alkyl radicals are directly united to carbonyl, as in the molecules of the ketones and aldehydes. As examples we may cite

$$\underset{\text{Pyruvic Acid.}}{CH_3\text{-}CO\text{-}CO\text{-}O\text{-}H} \qquad \underset{\text{Acetacetic Ether.}}{CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}O\text{-}C_2H_5} \quad [491]$$

Compare pyruvic acid with oxalic acid, and the acid of the compound ether with malonic acid [482].

Substitution of Sulphur Radicals.

477. **Sulphur Compounds.** — These compounds correspond very closely to the oxygen compounds we have just studied, as is shown by the following table, in which the names and symbols of the two classes are side by side.

Methyl Alcohol,	$CH_3\text{-}O\text{-}H$	Methyl Mercaptan,	$CH_3\text{-}S\text{-}H$
Acetic Aldehyde,	$CH_3\text{-}CO\text{-}H$	Sulphaldehyde,	$CH_3\text{-}CS\text{-}H$
Acetic Acid,	$CH_3\text{-}CO\text{-}O\text{-}H$	Thiacetic Acid,	$CH_3\text{-}CO\text{-}S\text{-}H$
Methyl Ether,	$CH_3\text{-}O\text{-}CH_3$	Methyl Sulphide,	$CH_3\text{-}S\text{-}CH_3$.

Certain differences, however, are to be noted. 1st. The mercaptans are more acid than the alcohols. Thus,

$$2CH_3\text{-}SH + Hg_2O = (CH_3)_2\text{-}S_2\text{-}Hg + H_2O. \quad [476]$$

36. There is a tendency to form polysulphides (§ 175).

$$2C_2H_5\text{-}Na + I_2 = (C_2H_5)_2S_2 + 2NaI. \quad [477]$$

Sodic Ethoxide. Ethyl Disulphide.

37. The sulphur can be oxidised, when a class of products results called sulpho-acids. These compounds may be better classified as formed from the hydrocarbons by the substitution of the radical $-SO_2\text{-}O\text{-}H$ for one or more hydrogen atoms. Thus may be derived

$CH_3\text{-}SO_2\text{-}O\text{-}H$ (Methyl Sulphonic) $CH_2(SO_2\text{-}O\text{-}H)_2$ (Methylene Disulphonic) $CH(SO_2\text{-}O\text{-}H)_3$ (Methine Trisulphonic)

$$CH_3I + K_2SO_3 = K\text{-}O\text{-}SO_2\text{-}CH_3 + KI. \quad [478]$$

Compare §§ 178 and 182.

So, also, the group $-SO\text{-}O\text{-}H$ may be substituted.

Substitution of Nitrogen Radicals.

478. **Amines, Amides, Imides, Nitriles,** may be regarded as derived by replacing one or more hydrogen atoms of one or more molecules of a hydrocarbon by the radicals $\overset{\text{I}}{N}H_2$, $\overset{\text{II}}{N}H$, or $\overset{\text{III}}{N}$; but they may also, and to a greater advantage, be studied as related to the molecule NH_3, and as formed from it by replacing one or more of the hydrogen atoms of a single or of several molecules of ammonia by various hydrocarbon radicals. From this point of view they have already been studied in as great detail as is possible in this work, and the student is advised to review in this connection §§ 317 to 327, in order to include these compounds in the general scheme which we have adopted for classifying organic products.

479. **Cyanogen, the Cyanides, the Cyanates, etc.,** may, in a similar way, be regarded as formed by the substitution of atoms of nitrogen, acting either as trivalent or quinquivalent radicals for a corresponding number of atoms of hydrogen; but these products are best studied as compounds of the well-marked and highly characteristic radical cyanogen. From this point of view the more important of them have already been described, and a review of §§ 444 to 451 will enable the student to assign them their proper place in the present scheme. We add here a few reactions which indicate the exist-

ence of two different radicals, in one of which nitrogen is trivalent and in the other quinquivalent, that is, $-C{\equiv}N$ and $C{\equiv}N-$.

$$KCN + CH_3,K{=}O_2{=}SO_2 = K_2{=}O_2{=}SO_2 + \underset{\text{Boils at 98°.}}{CH_3{-}C{\equiv}N}. \qquad [495]$$

$$CH_3{-}C{\equiv}N + 2\,H_2O = \underset{\text{Acetic Acid.}}{CH_3{-}CO{-}O{-}H} + NH_3. \qquad [496]$$

Compare with these

$$AgCN + CH_3I = AgI + \underset{\text{Boils at 79°.}}{CH_3{-}N{\equiv}C}. \qquad [497]$$

$$CH_3{-}N{\equiv}C + 2\,H_2O = \underset{\text{Methylamine.}}{CH_3{-}NH_2} + \underset{\text{Formic Acid.}}{H{-}C{=}O{-}O{-}H}. \qquad [498]$$

In methylamine the methyl group is undoubtedly attached to a nitrogen atom, while in acetic acid it is as undoubtedly united to a carbon atom. Hence, reasoning back, we conclude that the same relations must obtain in the two isomeric products of [497] and [495], and, if so, the above conclusion in regard to the two modifications of cyanogen at once follows. Hence, there must be two modifications of hydrocyanic acid, namely, $H{-}C{\equiv}N$ and $H{-}N{\equiv}C$, and the two appear to be mixed in the common acid. A similar isomerism appears in the cyanates and sulphocyanates. We have already described the potassic cyanates and sulphocyanates (§§ 451 and 452); but the most interesting compounds of this class are those of the alkyl radicals, the ethers so called, and the investigation of the many wonderful transformations of which these bodies are susceptible was one of the most important steps in the progress of organic chemistry.

From potassic cyanate, prepared by [409], we obtain isocyanic ether by the following reaction:—

$$\underset{\text{Distilled together.}}{KOCN + K,C_2H_5{=}O_2{=}SO_2} = K_2{=}O_2{=}SO_2 + \underset{\text{Isocyanic Ether.}}{(C_2H_5)OCN}. \qquad [499]$$

Compare now

$$HOCN + 2\,K{-}O{-}H = K_2{=}O_2{=}CO + H,H,H{\equiv}N. \qquad [500]$$

$$(C_2H_5)OCN + 2\,K{-}O{-}H = K_2{=}O_2{=}CO + \underset{\text{Ethylamine.}}{H,H,C_2H_5{\equiv}N}. \qquad [501]$$

So also

$$(C_2H_5)OCN + 2\,K{-}O{-}C_2H_5 = K_2{=}O_2{=}CO + \underset{\text{Triethylamine.}}{(C_2H_5)_3{\equiv}N}. \qquad [502]$$

$$C_2H_5OCN + \underset{\text{Acetic Acid.}}{H{-}O{-}C_2H_3O} = \underset{\text{Ethylacetamide.}}{H,C_2H_5,C_2H_3O{=}N} + CO_2. \qquad [503]$$

On the other hand, by acting on sodic ethylate with chloride of cyanogen, we obtain an isomer of isocyanic ether, which sustains very different relations,

$$Na\text{-}O\text{-}C_2H_5 + CNCl = NaCl + \underset{\text{Cyanic Ether.}}{(C_2H_5)OCN},$$

and then,

$$\underset{\text{Cyanic Ether.}}{(C_2H_5)OCN} + 2\,K\text{-}O\text{-}H + H_2O = C_2H_5\text{-}O\text{-}H + K_2CO_3 + NH_3.$$

When now we analyze these reactions, it is quite evident that the two isomers have the structure indicated by the following symbols:—

$$\underset{\text{Isocyanic Ether.}}{O\text{=}C\text{=}N\text{-}C_2H_5} \qquad\qquad \underset{\text{Cyanic Ether.}}{N\text{≡}C\text{-}O\text{-}C_2H_5}$$

Although in these symbols no difference appears in the quantivalence of N, yet it will be noticed that the associations of the alkyl radical differs in these two bodies as in [495] and [497]. Moreover, it will be noticed that isocyanic ether is an amide, and all the reactions [500 to 503] become intelligible from this point of view.

A similar relation to that just described we find between the sulphocyanic ethers and the so-called mustard oils. Thus,

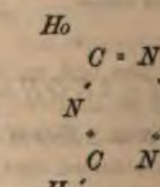
$$\underset{\text{Ethyl Mustard Oil.}}{S\text{-}C\text{=}N\text{-}C_2H_5} \qquad\qquad \underset{\text{Ethyl Sulphocyanate.}}{N\text{≡}C\text{-}S\text{-}C_2H_5} \qquad [504]$$

The natural mustard oil is a similar compound, containing the unsaturated radical allyl, C_3H_5.

$$\underset{\text{Oil of Mustard.}}{S\text{-}C\text{=}N\text{-}(CH_2\text{-}CH\text{-}CH_2)} \qquad [505]$$

Lastly, we add the following symbols, as examples of very complex structures which may be built up from carbon and nitrogen atoms:—

Cyanuric Acid, $C_3N_3O_3H_3$ or



Dicyandiamide, $NH\text{-}C\text{=}(NH)_2\text{=}C\text{=}NH$

Guanidine, $NH\text{-}C\text{=}(NH_2)_2$

Replacements by NO_2.

Compounds of this univalent group have been made by the general reaction

$$CH_3I + AgNO_2 = CH_3NO_2 + AgI; \qquad [506]$$

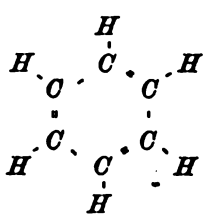
but such compounds are as yet of little importance in the fat series.

Replacements by Metals.

480. **Metallic Compounds.** — Here belong the various compounds of the metals with hydrocarbon radicals, which have already been described under their respective divisions.

HYDROCARBONS OF THE AROMATIC SERIES, AND THEIR DERIVATIVES. — CLOSED CHAINS.

481. **Benzol.** — This well-known hydrocarbon, which is the basis of a large class of compounds, is one of the chief products of the distillation of coal tar. We have no certain evidence in regard to its molecular structure, and differences of opinion are entertained, but the remarkable relations of the compound are so well explained by the hypothesis of Kekulé, according to which the carbon atoms are arranged as represented by the accompanying diagram, that we shall



[507]

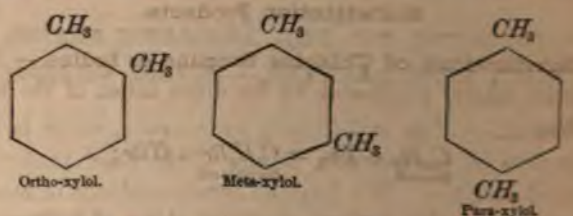
adopt this theory as the best mode of classifying the facts, without, however, regarding it as anything more than the conventional form of a working hypothesis. When, therefore, in this connection, we write C_6, it must be assumed that the carbon atoms are grouped as indicated.

By substituting for H in benzol different hydrocarbon radicals, we obtain a series of homologues of benzol, some of which are associated with it in the products of the distillation of coal tar. The second

member of this homologous series, C_7H_8, is called toluol, and is sim
methylbenzol, or $C_6H_5\text{-}CH_3$. Of course, the radical can be attach
to any one of the carbon atoms, but, according to the principle alre
stated (§ 455), this variation would determine no real difference
structure, although it might make an apparent difference on our c
ventional diagram. The second member of the series, C_8H_{10}, may
either

$$\underset{\text{Ethylbenzol.}}{C_6H_5\text{-}C_2H_5} \qquad \text{or} \qquad \underset{\text{Dimethylbenzol.}}{C_6H_4\text{=}(CH_3)_2}$$

The first of these bodies, like methylbenzol, admits of no isomeric
but the second, which is usually called xylol, gives three isom
according to the relative position of the two radicals on the hexagon



Ortho-xylol. Meta-xylol. Para-xylol.

Whenever two only of the hydrogen atoms of benzol are replaced, th
same nomenclature is used, and the isomers are called *ortho* when th
radicals are on adjacent links, *meta* when on alternate links, *par*
when on opposite links.

It is obvious that the carbon atoms of the hydrocarbon radi
form an accessory chain to the main group, and this subordinate chai
is called a *side chain*. The side chain may be either a saturated alip
radical, as in toluol or xylol, or it may be an unsaturated radical, a
in styrol, $C_6H_5\text{-}C_2H_3$, or even it may be another aromatic group, as i
diphenyl, $C_6H_5\text{-}C_6H_5$.

The synthesis of benzol has been accomplished by passing acetylen
through a heated porcelain tube.

$$3C_2H_2 = C_6H_6.$$

And from benzol we can pass to the higher hydrocarbons of the
aromatic series by what is known as Fittig's reaction.

$$C_6H_5Br + Na_2 + CH_3I = C_6H_5\text{-}CH_3 + NaBr + NaI$$

DERIVATIVES FROM THE HYDROCARBONS. — WITH CLOSED CHAINS.

482. **Addition Products.** — Since in the hexagonal ring of benzol there are three double bonds, we should infer that the molecule was unsaturated, and capable of uniting with six additional univalent atoms or radicals. But although such addition products are known, they are obtained with far less readiness than in the case of the olefines or acetylenes, and this circumstance has led to a question in regard to the hypothesis which requires us to assume their existence. Addition products may also result from additions to side chains when unsaturated.

Substitution Products.

483. **Substitutions of Chlorine, Bromine, or Iodine.** — Such substitutions are readily produced by the direct action of the haloid elements, thus,

$$\underset{\text{Benzol.}}{C_6H_6} + Br_2 = \underset{\text{Brombenzol.}}{C_6H_5Br} + HBr; \qquad [511]$$

and by continuing the action, successive atoms of hydrogen can be replaced in a similar way. With one atom of hydrogen replaced there can be no isomers; with two atoms replaced, there can be three isomers, as shown in § 481. With three replaced, there can be also three isomers, for if we number the six carbon atoms of the ring from one to six, we shall have three different relations according as we replace 1, 2, 3, 1, 2, 4, or 1, 3, 5; and these are the only essentially different combinations which we can make.

With the higher hydrocarbons of the aromatic series, which have side chains, we may replace either the hydrogen atoms of the ring or those of the side chains, and the first are more readily replaced than the last. According to Beilstein's law, chlorine or bromine atoms, as a general rule, go into the ring in the cold, especially in the presence of iodine, but not into the side chain except at temperatures above 110°.

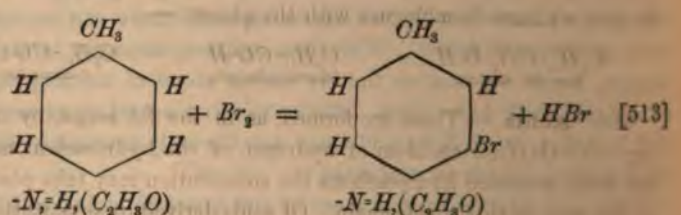
The two different associations which an atom of a halogen may have in such a hydrocarbon increases the number of possible isomeric forms. Thus, there may be four isomers of benzylchloride, C_7H_7Cl, one with the chlorine atom in the side chain, thus, $C_6H_5 \cdot CH_2Cl$, and three with the chlorine atom in the ring. When in the last association,

the chlorine atom and the radical CH_3 may have the three different relative positions on the ring shown in § 481. Replacements in the side chains follow the same laws as in the fat series. Such replacements, like those on open chains, can be easily dislodged, while radicals on the ring can be removed only with great difficulty, as by the action of metallic sodium or fusing with caustic alkali. Compare [510].

The following reactions will help to elucidate the principles we are discussing.

$$\underset{\text{Toluol.}}{C_6H_5\text{-}CH_3} + Br_2 = \underset{\text{Bromtoluol.}}{C_6H_4Br\text{-}CH_3} + HBr. \qquad [512]$$

In this reaction the bromine atom has replaced an atom of hydrogen on the ring. On this ring are now two radicals, namely, Br and CH_3, and they must have relatively to each other one of the three positions shown in § 481. The product is in fact a mixture of ortho- and para-bromtoluol. In these isomers the radicals are in the relative positions most readily assumed. In order to obtain the intermediate position of metabromtoluol we must first occupy the para position with an amide, and then the bromine will replace the hydrogen atom nearest to the amide radical, thus:—



[513]

If now we replace the amide by hydrogen, we have the isomer required.

Substitutions of Hydroxyl or Oxygen.

484. **Phenols.** — If we replace one hydrogen atom of benzol by Ho, we obtain Phenol, $C_6H_5\text{-}O\text{-}H$, a compound which is more familiarly known as Carbolic Acid, and whose structure admits of no isomerism. If, however, we replace two hydrogen atoms by Ho, the product, $C_6H_4{=}Ho_2$, is capable of three isomeric modifications, according to the relative position of the hydroxyl groups on the ring (§ 481).

The ortho form is called Pyrocatechin.
The meta form is called Resorcin.
The para form is called Hydrochinon.

The general term *Phenols* applies to all such compounds whose molecules have *Ho* united to the ring. In their structure they are allied to the tertiary alcohols, but they have the qualities of weak acids.

$$H\text{-}O\text{-}C_6H_5 + K\text{-}O\text{-}H = K\text{-}O\text{-}C_6H_5 + H_2O. \qquad [514]$$

485. **Alcohols.** — It is obvious that with toluol, or any other homologue of benzol, we may replace a hydrogen atom of the side chain by *Ho*, and that then we must have the complete structure of an alcohol. Thus $C_6H_5\text{-}CH_3$ gives $C_6H_5\text{-}CH_2\text{-}O\text{-}H$, benzoic alcohol. If now the *Ho* is transferred from the side chain to the ring, we shall have a phenol isomeric with the alcohol, which is itself capable of three modifications, according to the relative position of the *Ho* and CH_3. These isomeric bodies are called, according to the rules given in § 481, orthocresol, metacresol, paracresol. The alcohol gives an aldehyde and an acid, as in the fat series, thus: —

$C_6H_5\text{-}CH_2\text{-}O\text{-}H$	$C_6H_5\text{-}CO\text{-}H$	$C_6H_5\text{-}CO\text{-}O\text{-}H$
Benzoic Alcohol.	Benzoic Aldehyde, or Oil of Bitter Almonds.	Benzoic Acid.

So also we have homologues with the above: —

$C_9H_{11}\text{-}CH_2\text{-}O\text{-}H$	$C_9H_{11}\text{-}CO\text{-}H$	$C_9H_{11}\text{-}CO\text{-}O\text{-}H$
Cumylic Alcohol.	Cuminic Aldehyde.	Cuminic Acid.

486. **Acids.** — These are formed, as in the fat series, by substituting $\text{-}CO\text{-}O\text{-}H$ for an atom of hydrogen of the hydrocarbon molecule; but with aromatic hydrocarbons the substitution may take place either in the ring or in the side chain. Of acids derived by substitution in the ring, the most important and the simplest is benzoic acid, whose symbol has just been given. This body, formerly exclusively obtained by sublimation from gum benzoin, is now more frequently procured from hippuric acid, which is found abundantly in the urine of herbivorous animals. When hippuric acid is boiled with hydrochloric acid, the radical C_7H_5O in this amide changes place with *H* of *H-O-H*, and the products are glycocol and benzoic acid (§ 319).

If one of the hydrogen atoms in the ring of toluol, $C_6H_5\text{-}CH_3$, is replaced by $\text{-}CO\text{-}O\text{-}H$, the product will differ according to the relative position of the radicals methyl and carboxyl [508], and thus of toluylic acid, $CH_3\text{-}C_6H_4\text{-}CO\text{-}O\text{-}H$, there are three isomers. Still a fourth isomer

may result by replacing a hydrogen atom of the side chain instead of the ring. Thus we derive alphatoluylic acid, $C_6H_5\text{-}CH_2\text{-}CO\text{-}O\text{-}H$.

It is evident that through the side chains of the aromatic compounds relations of structure may be established similar to those in the fat series, and hence we might expect similar classes of acids. If the side chain is unsaturated, the product is an unsaturated acid, and an excellent example of such a compound is

Cinnamic Acid, $C_6H_5\text{-}CH\text{=}CH\text{-}CO\text{-}O\text{-}H$,

which differs from acrylic acid [481] only in having the radical C_6H_5 instead of H at the end of an otherwise open chain.

We may also have among the acids of the aromatic series the same distinctions between atomicity and basicity as in the fat series (§ 475). As before, the basicity depends on the number of carboxyl groups, $\text{-}CO\text{-}Ho$, while the atomicity is determined by the total number of hydroxyl groups. The following is an interesting isomeric group of monobasic but diatomic acids: —

Salicylic Acid,	The ortho form of $H\text{-}O\text{-}C_6H_4\text{-}CO\text{-}O\text{-}H$.
Metaoxibenzoic Acid,	The meta form of $H\text{-}O\text{-}C_6H_4\text{-}CO\text{-}O\text{-}H$.
Paraoxibenzoic Acid,	The para form of $H\text{-}O\text{-}C_6H_4\text{-}CO\text{-}O\text{-}H$.

Lastly, we may mention a most remarkable series of acids, which may be regarded as formed by replacing successively all the hydrogen atoms of benzol by carboxyl, and which therefore present every gradation from monobasic to hexabasic.

Benzol,			C_6H_6
Benzoic Acid,			$C_6H_5\text{-}(CO\text{-}O\text{-}H)$
Terephthalic Acid,	Isophthalic Acid,	Phthalic Acid,	$C_6H_4\text{=}(CO\text{-}O\text{-}H)_2$
Trimellitic Acid,	Trimesic Acid,	Hemimellitic Acid,	$C_6H_3\text{≡}(CO\text{-}O\text{-}H)_3$
Pyromellitic Acid,	Prehnitic Acid,	Mellophanic Acid,	$C_6H_2\text{=}(CO\text{-}O\text{-}H)_4$
			$C_6H\text{≡}(CO\text{-}O\text{-}H)_4$
Mellitic Acid,			$C_6\text{=}(CO\text{-}O\text{-}H)_6$

The three isomeric forms which are given above obviously result from a variation of the relative position of the carboxyl groups on the benzol ring.

487. **Ketones.** — As examples of compounds in the aromatic series corresponding to the ketones of the fat series we have

Benzophenone, $C_6H_5\text{-}CO\text{-}C_6H_5$ Acetophenone, $C_6H_5\text{-}CO\text{-}CH_3$

488. **Quinones** are a class of compounds peculiar to the aromatic series. They are formed by the oxidation of aromatic bodies, and are supposed to contain the radical $=[O_2]$, directly united by both bonds with the benzol ring. Quinone, $C_6H_4=[O_2]$, a volatile solid originally obtained by the oxidation of quinic acid found in cinchona bark, is the simplest of these bodies. When acted on by *HI*, a strong reducing agent, quinone yields hydroquinone, $C_6H_4=Ho_2$, and the fact that O_2 is thus replaced by Ho_2 seems to indicate that the oxygen atoms were united to the benzol ring by two, and not by all four, of their bonds, and hence that they must be united with each other as we have assumed. As hydroquinone has two radicals united to the benzol ring, it must be one of three possible isomers (§ 481); and if we can distinguish whether it is an ortho, meta, or para compound, we can determine the points of attachment of the oxygen radical. As it proves to be a para compound, it follows that the oxygen bonds are united at opposite sides of the ring.

Substitution of Sulphur Radicals.

489. **Sulphur Compounds** may be formed in the aromatic series, as in the fat series, after the same types as the oxygen compounds; but the most important compounds of this class are the sulpho-acids, which may be regarded as derived from sulphuric or sulphurous acids by replacing one of the hydroxyl groups by a benzol radical, thus:—

$$C_6H_6 + H_2{=}O_2{=}SO_2 = H\text{-}O\text{-}SO_2\text{-}C_6H_5 + H_2O. \qquad [515]$$

The product of this reaction, when fused with caustic potash, yields carbolic acid.

$$H\text{-}O\text{-}SO_2\text{-}C_6H_5 + 2\,KOH = \underset{\text{Phenol.}}{H\text{-}O\text{-}C_6H_5} + K_2{=}O_2{=}SO + H_2O. \qquad [516]$$

Thus these two reactions enable us to effect the synthesis of the phenols.

Substitution of Nitrogen Radicals.

490. **Nitro Compounds.** *Radical, NO_2.* — These compounds are very important, and more stable than in the fat series.

$$C_6H_6 + HNO_3 = \underset{\text{Nitrobenzol.}}{C_6H_5\text{-}NO_2} + H_2O. \qquad [517]$$

$$C_6H_5NO_2 + HNO_3 = \underset{\text{Dinitrobenzol.}}{C_6H_4{=}(NO_2)_2} + H_2O. \qquad [518]$$

These compounds cannot, however, be made by the action of $AgNO_2$ on C_6H_5I.

491. **Amido Compounds.** *Radical*, NH_2. — The amido compounds can be obtained from the nitro compounds by reduction.

$$\underset{\text{Nitrobenzol.}}{C_6H_5NO_2} + 3H_2 = \underset{\text{Aniline.}}{C_6H_5\text{-}NH_2} + 2H_2O. \qquad [519]$$

They are capable of the following transformations : —

1st. The hydrogen atoms of NH_2, the side chain in aniline, can be readily replaced by alkyl radicals.

$$\underset{\text{Aniline.}}{C_6H_5\text{-}NH_2} + CH_3I = \underset{\text{Methylaniline.}}{C_6H_5\text{-}NH\text{-}CH_3} + HI.$$

So also dimethylaniline, $C_6H_5\text{-}N(CH_3)_2$. If methylaniline is heated, the radical CH_3 passes from the side chain to the ring, thus : —

$$C_6H_5\text{-}NH\text{-}CH_3 = \underset{\text{Toluidine.}}{(C_6H_4\text{-}CH_3)\text{-}NH_2}. \qquad [520]$$

This transfer of atoms or radicals from one part of a molecule to the other, in this case from the side chain to the ring, without breaking up the carbon nucleus, is not uncommon, and may be called *atom roving*.

2d. The hydrogen atoms of NH_2 may be replaced by aromatic radicals after substituting K in the side chain.

$$C_6H_5\text{-}NH\text{-}K + C_6H_5Br = \underset{\text{Diphenylamine.}}{(C_6H_5)_2\text{-}NH} + KBr. \qquad [521]$$

3d. The hydrogen atoms of NH_2 may be replaced by acid radicals.

$$C_6H_5\text{-}NH_2 + (C_2H_3O)\text{-}Cl = \underset{\text{Phenylacetamide or Acetanilide.}}{C_6H_5\text{-}NH\text{-}C_2H_3O} + HCl. \qquad [522]$$

By the incomplete reduction of nitro compounds, products may be obtained which are intermediate between these and those of the amido class. Thus we have

Nitrobenzol,	$C_6H_5\text{-}NO_2$
Azoxibenzol,	$C_6H_5\text{-}(\overset{O}{N}\text{-}N)\text{-}C_6H_5$
Azobenzol,	$C_6H_5\text{-}N\text{=}N\text{-}C_6H_5$ [523]
Hydrazobenzol,	$C_6H_5\text{-}NH\text{-}NH\text{-}C_6H_5$
Amidobenzol,	$C_6H_5\text{-}NH_2$

These compounds are comparatively stable, except hydrazobenzol, which under the influence of acid undergoes the following change : —

$$C_6H_5\text{-}NH\text{-}NH\text{-}C_6H_5 = \underset{\text{Diamido-diphenyl.}}{NH_2\text{-}C_6H_4\text{-}C_6H_4\text{-}NH_2}. \qquad [524]$$

492. **Diazo Compounds.** *Radical,* $\text{-}N{=}N\text{-}$ or $N{\equiv}N$. — If the nitrate of phenylammonium is acted on by nitrous acid, we have the following reaction : —

$$(H_3, C_6H_5{\equiv}N)\text{-}NO_3 + HNO_2 = \underset{\text{Nitrate of Diazobenzol.}}{C_6H_5\text{-}N_2\text{-}NO_3} + 2\,H_2O. \qquad [525]$$

The nitrate of diazobenzol is very unstable, and undergoes the following singular transformations : —

$$C_6H_5\text{-}N_2\text{-}NO_3 + H_2O = \underset{\text{Phenol.}}{C_6H_5\text{-}O\text{-}H} + N_2 + HNO_3. \qquad [526]$$

$$\underset{\text{Alcohol.}}{C_6H_5\text{-}N_2\text{-}NO_3} + \underset{}{C_2H_5\text{-}O\text{-}H} = \underset{\text{Benzol.}}{C_6H_6} + N_2 + HNO_3 + \underset{\text{Aldehyde.}}{C_2H_4O}. \qquad [527]$$

The reaction [526] gives an important method of making phenols, and both this and [527] illustrate a class of reactions which have been most useful in the study of the aromatic compounds.

493. **Hydrazines.** — Further evidence of the structure of the nitrogen radical in the diazo compounds is furnished by the fact, that under the action of nascent hydrogen these bodies yield products called hydrazines, whose relations are best explained on the assumption that they contain the group $(NH_2\text{-}NH)\text{-}$. Their formation is illustrated by the following reactions : —

$$\underset{\text{Sulphite of Diazobenzol.}}{(C_6H_5\text{-}N_2)_2{=}SO_3} + 2\,H_2 = \underset{\text{Sulphite of Phenylhydrazine.}}{(C_6H_5, H{=}N\text{-}NH_2)_2{=}SO_3}. \qquad [528]$$

Also we have [523]

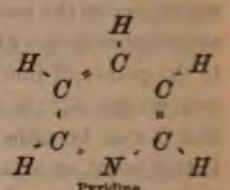
$$(C_6H_5)_2{=}N\text{-}NO + 4\,H = (C_6H_5)_2{=}N\text{-}NH_2 + H_2O. \qquad [529]$$

Similar compounds have also been made from the fat series.

Chains containing Nitrogen.

494. **Pyridine** (NC_5H_5) is a colorless liquid soluble in water, derived from the products of the distillation of bones, bituminous shales, natural alkaloids, and other nitrogenized materials, and bears similar relations to the so-called pyridine bases that benzol bears to the aromatic hydrocarbons, and is susceptible of similar transformation. The study of these relations has led to the theory that it has a molecular

structure similar to benzol, with the exception that the ring which forms the nucleus of the molecule contains an atom of nitrogen, as in the graphic symbol at the side of the page. Pyridine, like NH_3, combines directly (as an addition) to acids to form salts. Thus,

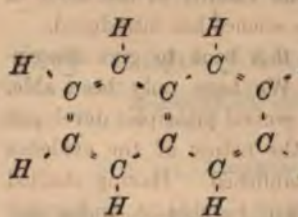

Pyridine.

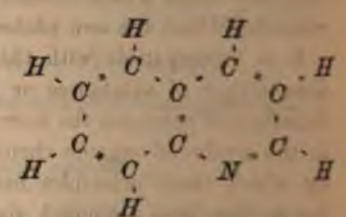
$$NC_5H_5 + HCl = HClNC_5H_5;$$

and, as in the formation of ammonium salts (§ 322), we assume that the nitrogen atom of the pyridine ring becomes quinquivalent, and attaches to itself not only the chlorine, but also the hydrogen atom of the acid molecule. Picoline, a base associated with pyridine, bears the same relation to it that toluol bears to benzol; that is, picoline is methylpyridine, $NC_5H_4\text{-}CH_3$. Here methyl replaces one of the hydrogen atoms of the ring. These atoms may also be replaced by various radicals. Thus we have $(NC_5H_4)\text{-}CO\text{-}O\text{-}H$, pyridine carboxylic acid, a compound capable of three isomeric modifications, according to the position of the carboxyl group on the ring with reference to the nitrogen, and it can easily be seen that the pyridine group presents infinite possibilities of substitutions, additions, and transformations.

Complex Chains.

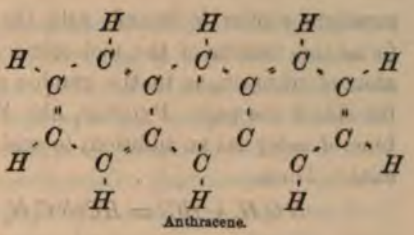
495. **Naphthaline, Anthracene, etc.** — The following graphic symbols best represent the chemical relations of certain very remarkable compounds which are among the products of the distillation of coal tar. As will be seen, they may be regarded as formed by the coalescing of two or more benzol rings.


Naphthaline.


Chinoline.

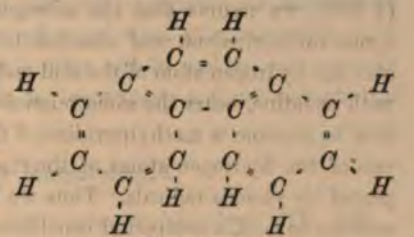
It will be noticed that chinoline is related to naphthaline in the same way that pyridine is related to benzol. It will be noticed, moreover, that while one substitution of a hydrogen atom on the ring gives no isomers in the case of benzol, a similar substitution gives two iso-

mers in the case of naphthaline, depending on the position of the replacing radical with reference to the points of junction of the two rings; for it is evident that it can be either adjacent to this point, or separated from it by one atom of hydrogen. These forms are distinguished by the letters α and β.



Anthracene.

Anthracene and phenanthrene are two isomeric hydrocarbons from the same source, whose molecular structure is represented by the conventional diagrams at the side of the page.



Phenanthrene.

Alizarine is related to anthracene thus: —

$C_{14}H_{10}$ Anthracene. $C_{14}H_8O_2$ Anthraquinone. $HO_2 \cdot C_{14}H_5[O_2]$ Anthraquinonic Acid, or Alizarine.

This most important dye-stuff is now manufactured from anthracene, in large quantities, by a process which was discovered by following out the indications of the theory of the molecular structure of this long-known product of organic nature; and this *synthesis* of alizarine is not only one of the most remarkable achievements of modern chemistry, but is also a direct corroboration of the validity of the mode of reasoning which the new philosophy of the science has introduced.

It is incompatible with the design of this book to give descriptions either of substances or processes. We have only been able, therefore, to point out the more important general principles developed in the study of organic chemistry, and the nature of the evidence by which these principles have been established. Having studied the outline here presented, the student will be able to understand the descriptions of investigations in this department of chemistry, which are being constantly published in the leading chemical journals; and he is earnestly advised to extend his studies to original papers of marked excellence. By studying the details in a few conspicuous and characteristic examples, he will gain a far more accurate

conception of the methods and modes of thought by which this field of science has been so successfully cultivated, than can possibly be obtained from a text-book. But no study of books can give a living, personal knowledge of any experimental science, and this is especially true of organic chemistry, in which the forms of expression are so obviously conventional. These forms are of no value in themselves. They are mere tools, and only serve their legitimate purpose in the hands of the true student of nature, whom they help to grasp the phenomena he observes. He who proposes to study organic chemistry experimentally must learn the use of these tools, and, for such students, the outline of the subject we have given may serve as an introduction to this department of chemical science.

Physiological Chemistry.

496. The hydrocarbon compounds and their derivatives may also be studied as products of the vital processes of plants and animals; and when studied from this point of view they become the basis of important branches of knowledge, known as animal chemistry, physiological chemistry, phytochemistry, or agricultural chemistry, according to the field embraced. Animal chemistry has a special interest, on account of its bearings on medicine. But, although the subject-matter is the same, the aims of study in these departments are so very different from the investigation of molecular structure, that they have little in common with what is now generally understood as organic chemistry. The study of these subjects has developed no new principles of chemical philosophy, and the details are so numerous that it would be impossible to give even a summary of them in a work like this. We can only, therefore, point out these subjects as well established, although somewhat indefinite, branches of chemistry.

497. **Fermentation.** — This term is applied to a number of remarkable chemical processes, which depend upon the life and growth of a very low order of organized beings, belonging chiefly to the vegetable kingdom. These organisms are the efficient part of what is called the ferment, or yeast. The fermenting material is their appropriate food, and the products of fermentation are in some unknown way determined by the vital process, different ferments — that is, different organisms — producing different results. Moreover, we can frequently distinguish between the growth and propagation of these

organisms, and the normal vital process by which the products of fermentation are evolved; the first requiring the presence of certain materials, chiefly albuminous, which otherwise take no part in the chemical change. The germs of these living beings are widely diffused, floating even in the atmosphere, and begin at once to grow as soon as a fermentable liquid and the right temperature supply the conditions of active life. Fermentation, therefore, may set in without the apparent addition of any ferment, and, on the other hand, the change may be prevented by sealing up the material in air-tight cans previously heated to such a temperature as will insure the destruction of all living germs. The principal modes of fermentation are: —

1st. Alcoholic fermentation, caused by a fungus, the *Saccharomyces cerevisiæ*, commonly called Yeast, which converts glucose into ethylic alcohol and carbonic anhydride, forming, however, at the same time, small amounts of amylic and other alcohols, besides traces of succinic acid and glycerine.

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2. \qquad [530]$$

2d. Acetous fermentation, induced by the *Mycoderma vini*, by which alcohol is changed into vinegar.

3d. Lactic fermentation, in which the *Penicillium glaucum* converts saccharine materials into lactic acid.

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = 2\,\underset{\text{Lactic Acid.}}{C_3H_6O_3}. \qquad [531]$$

4th. Butyric fermentation, supposed to be caused by an animal, in which lactic acid, formed as above, is changed into butyric acid.

$$2\,C_3H_6O_3 = C_4H_8O_2 + 2\,CO_2 + 2\,H\text{-}H. \qquad [532]$$

5th. Mucous fermentation, which sugar undergoes under the influence of the "mucous ferment," giving rise to the escape of carbonic anhydride and hydrogen, and the formation of mannite, together with a peculiar gum and a mucilaginous substance.

498. **Conclusion.** — The different forms of fermentation are but lower modes of the manifestation of that obscure power by which animals and plants not only prepare the materials of their tissues, but also secrete from their organisms the various products of their vital processes. As has been shown, we have been able, to a limited extent, to achieve in our laboratories the same results, and we can see no limit to our synthetical methods. Nevertheless, we have not been

able as yet to produce any of the materials which make up the great mass of the tissues of all organized beings; and this, which is true of the gum, starch, and woody fibre of plants, is true to a still greater degree of such materials as albumen, caseine, gelatine, fibrine, etc., which are the main constituents of the animal body. In regard to the composition of these nitrogenized compounds we have no knowledge except that which may be obtained by ultimate analysis; and although we have every reason to believe that future investigation will reveal their molecular constitution, so far as they are simple chemical compounds, yet in most cases the *substance* of these bodies cannot be isolated from the organic structure which determines in a great measure their distinctive qualities; and not only has man never been able to make the simplest organic cell, but the whole process of its growth and development is utterly beyond the range of his conceptions. Moreover, even in regard to those simpler products of organic life which we have been able to reach by synthesis, we have no knowledge of the processes by which they are formed in organic nature.

The vegetable kingdom is a great laboratory, in which the sun's rays manufacture from the gases of the atmosphere, and from a few earthy salts of the soil, the different materials which the organic builders employ. The animal, unlike the plant, has not the power of forming the substance of its tissues from inorganic compounds, but it receives from the vegetable laboratory the materials required ready formed. It transmutes these products into a thousand shapes in order to adapt them to its wants; but its peculiar province is to assimilate and consume, not to produce. The nitrogenized compounds just referred to are the portion of its food which supplies the constant waste attending all the vital processes. The non-nitrogenized starch and sugar, although they form the greater part of its food, are never incorporated into the tissues of the body, but are merely the fuel by which its temperature is maintained. Here, however, chemistry stops, and the science of physiology begins.

In closing this summary of facts, we must remind the student that, as we stated in the Introduction, we have made no attempt at completeness. Although the chief characteristics of all the chemical elements have been illustrated, yet important classes of compounds have been necessarily left unnoticed, and this is especially true in the last division of the book. Organic chemistry presents such a vast array of facts, that the attempt to comprehend the whole field would

simply lead to confusion, and serve no useful end. We have, therefore, limited ourselves to those classes of compounds whose molecular structure is best understood, and our great object has been to illustrate the methods by which a knowledge of this structure has been reached. It is by these methods that the new philosophy of chemistry is chiefly distinguished from the old, and to them we shall especially direct the student's attention in the questions which follow. He should not content himself, however, with simply answering these questions, but, by an exhaustive study of all the reactions which have been given, and by a constant use of graphic symbols, endeavor to become imbued with the spirit of the philosophy which it has been the object of this book to illustrate.

QUESTIONS AND PROBLEMS.

Carbon and Oxygen.

1. Deduce the atomic weight of carbon, and state the facts and principles on which the conclusion is based.

2. When the product of the combustion of coal is CO, what proportion of the calorific power of the fuel is lost? (§ 66.)

3. Is the combination of CO_2 with additional carbon in passing through a mass of incandescent coal attended with an evolution or an absorption of heat? Estimate the amount of the effect produced.

4. Illustrate by examples, and seek to establish by reactions or other facts, the carboxyl theory of the constitution of organic acids.

Carbon and Nitrogen.

5. On what facts is the symbol of cyanogen gas based?

6. In what respects does HCy resemble, and how does it differ from, the hydrogen acids of the chlorine group?

7. What is the distinction between the two classes of double metallic cyanides?

8. Represent by graphic symbols the constitution of several of the polymeric compounds of cyanogen, including the ferro- and ferri-cyanides of potassium.

9. Urea, when in solution in water, changes into ammonic carbonate. Write the reaction.

Carbon and Hydrogen.

10. In what sense do structural symbols represent the molecular structure of a compound? What is meant by saying that they "generalize" or "prefigure" possible reactions?

11. In what respects are the aims and methods in organic chemistry different from those in mineral chemistry?

12. Explain the distinction between an open and a closed chain of carbon atoms.

13. How many essentially different modes of grouping are possible with an open carbon chain of four atoms, assuming that no atom is united to any one of its neighbors by more than one bond? How many, with a skeleton of five atoms, etc.?

14. Deduce the general symbol of a hydrocarbon formed around a nucleus of carbon atoms united as described in the last example, and show that the number of hydrogen atoms in such a compound depends only on the number of the carbon atoms, and is independent of the mode of grouping.

15. An addition of one atom of carbon to the nucleus involves the addition of how many atoms of hydrogen to the hydrocarbon? Define an homologous series.

16. How many essentially different modes of grouping are possible with an open carbon chain of four atoms, when two of the atoms are united by a double or by a treble bond? How many, with a skeleton of five atoms?

17. What is the effect of increasing the number of bonds between the carbon atoms of the nucleus on the number of hydrogen atoms in the corresponding hydrocarbon molecule? Define an isologous series.

18. Is the number of H atoms in the molecule of a hydrocarbon necessarily an even number?

19. Make a table of the possible hydrocarbons in series of homologues and isologues. Why is it that such a table does not present all the possibilities?

20. How many essentially different modes of grouping are possible with the hydrocarbons C_6H_{12}, C_6H_{10}, and C_6H_8?

21. What is the distinction between a saturated and a non-saturated compound? Illustrate by the relations of the paraffines, olefines, and acetylenes.

22. Why does a great interest attach to methods of synthesis in organic chemistry?

23. How can the synthesis of a hydrocarbon be effected? Take, as examples, C_2H_2 and C_3H_6.

24. Illustrate the meaning of the terms *addition products* and *substitution products*.

25. By what methods may compounds be obtained in which one or more atoms of chlorine, bromine, or iodine are substituted for a corresponding number of hydrogen atoms of a hydrocarbon?

26. Describe the feature in the structure of the three isomers of butyl, C_4H_9, to which the respective names [432] are applied.

27. The compound $C_2H_6Cl_2$ has four isomers. Point out the peculiar feature in the structure of each. [434.]

28. Define the terms *alcohol*, *glycol*, *glycerine*, *aldehyde*, *ketone*, and point out the peculiar feature in the structure of each of these classes of compounds. What is the characteristic feature in the structure of an organic acid?

29. Define the three classes of alcohols, and describe their characteristics of structure. By what reactions may the three be distinguished?

30. How may the synthesis of ordinary alcohol from elementary substances be effected?

31. What relation do the different classes of ethers sustain to the alcohols? [451 to 455.]

32. Explain the use of the term *carbinol*, and the advantages from adopting it.

33. Do the reactions given in §§ 469 and 470 establish the structure of the aldehydes and ketones?

34. Explain the relation of pinakone and pinakoline to ketone.

35. By what general reactions may acids be obtained [467, 468, and 469]?

36. What classes of compounds may be derived from acids by simple replacements? [470 to 473.]

37. On what does the basicity of an acid depend, and how may it be defined? Give characteristic examples of monobasic, dibasic, and tribasic acids.

38. Explain fully the relations between a monobasic acid, an aldehyde, and a primary alcohol.

39. How may a monobasic acid be converted into an alcohol?

40. By what general series of reactions can we pass from one fat acid to the next higher, and from one alcohol to the next higher in the same series?

41. Write a series of reactions by which butyric acid may be made from elementary substances.

42. Parallel to the series of fat acids is a series of unsaturated acids, of which acrylic acid is the first member. Make a table showing the relations of these two classes of compounds. How may a compound of the acrylic series be converted into the corresponding compound of the fat series?

43. Explain the relations of succinic and isosuccinic acid, and show that with dibasic acids isomerism may result from two different causes.

44. Discuss the structure of fumaric and maleic acid, and show that it is best explained on the assumption that one of the atoms of carbon is bivalent.

45. Explain the structural features on which atomicity and basicity depend, and give examples of acids whose atomicity is greater than the basicity, including lactic acid, malic acid, tartaric acid, and citric acid.

46. Point out the difference of structure between lactic and paralactic acid, and make clear the relations on which the isomerism depends.

47. Define and illustrate by examples the terms *aldehyde* and *ketone acids*.

48. Compare the sulphur with the corresponding oxygen compounds, and point out the change of relations which the substitution of sulphur for oxygen produces.

49. What is the evidence that the radical *CN* in *K-CN* differs from its isomer in *Ag-NC*? [495 to 498.]

50. Compare isocyanic ether and cyanic ether, and give the evidence of a structural difference between these two isomers. Trace back this difference to the bodies from which the two products are obtained. To what class of compounds does isocyanic ether belong? What must be the structure of common potassic cyanide and potassic cyanate? How is the formation of urea from ammonic cyanate thus explained?

51. Explain the relation of the sulphocyanates and the mustard oils.

52. Assuming that the benzol ring is a closed chain, as represented by [507], can you unite the carbon atoms symmetrically by the same number of bonds in any other way? If C_6H_6 forms an open chain, how could the carbon atoms be grouped?

53. The homologue of benzol, C_8H_{10}, is capable of what isomeric modification? Explain the relations of ortho, meta, and para compounds among the aromatic isomers.

54. Explain the distinction between the ring and the side chain.

55. Discuss the possibilities of isomerism in each of the three substitution products monobrombenzol, dibrombenzol, tribrombenzol, and tetrabrombenzol. Show that by numbering the carbon atoms of the ring the several possibilities may be easily expressed.

56. Give Beilstein's law, with an example of its application. [512.]

57. How many isomers of C_7H_7Br are possible? How may they be obtained?

58. What is the structure of a phenol, and what are the relations of these compounds?

59. Write the graphic symbols of the three isomeric modifications of $C_6H_4{=}Ho_2$.

60. Compare the relations of benzoic alcohol, benzoic aldehyde, and benzoic acid with the similar relations in the fat series, and show that the transfer of the hydroxyl group from the side chain to the ring determines an entire change of relations. What are the three isomers of benzoic alcohol thus produced?

61. Write the reaction by which benzoic acid is made from hippuric acid. (§ 319.)

62. Give the graphic symbols of the three isomers of toluylic acid.

63. Point out the relations of cinnamic to acrylic acid.

64. Show that salicylic acid and its isomers illustrate the distinction between atomicity and basicity. Why are there three, and only three isomers?

65. What is supposed to be the characteristic feature in the structure of the quinones? What is the evidence on which the opinion rests? Write the graphic symbol of the quinone $C_6H_4O_2$. What is the evidence for the position you give to the oxygen atoms?

66. How may phenol be prepared from benzol? What is the nature of the compound which forms the intermediate step in this process?

67. Can the nitrobenzols be regarded as nitrites? (§ 310.)

68. Compare [519] with the production of hydroquinone, and consider whether we might not reason, as in § 488, in regard to the relation of O_2 in the group NO_2.

TABLE I.

FRENCH MEASURES.

Measures of Length.

1 Kilometre	=	1000 Metres.	1 Metre	=	1.000 Metre.
1 Hectometre	=	100 "	1 Decimetre	=	0.100 "
1 Decametre	=	10 "	1 Centimetre	=	0.010 "
1 Metre	=	1 "	1 Millimetre	=	0.001 "

			Logarithms.	Ar. Co. Log
1 Kilometre	=	0.6214 Mile.	9.7933 712	0.2066 188
1 Metre	=	3.2809 Feet.	0.5159 930	9.4840 070
1 Centimetre	=	0.3937 Inch.	9.5951 742	0.4048 258

The metre is one ten-millionth of a quadrant of the globe.

Measures of Volume.

1 Cubic Metre	$\overline{m.}^3$	=	1000.000 Litres.
1 Cubic Decimetre	$\overline{d.m.}^3$	=	1.000 "
1 Cubic Centimetre	$\overline{c.m.}^3$	=	0.001 "

		Logarithms.	Ar. Co. Log.
1 Cubic Metre	= 35.31660 Cubic Feet.	1.5479 790	8.4520 210
1 Cubic Decimetre	= 61.02709 Cubic Inches.	1.7855 226	8.2144 774
1 Cubic Centimetre	= 0.06103 " "	8.7855 226	1.2144 774
1 Litre	= 0.22017 Gallon.	9.3427 581	0.6572 419
1 Litre	= 0.88066 Quart.	9.9448 083	0.0551 917
1 Litre	= 1.76133 Pints.	0.2458 407	9.7541 593

FRENCH WEIGHTS.

1 Kilogramme	= 1000 Grammes.	1 Gramme	= 1.000 Gramme.		
1 Hectogramme	= 100 "	1 Decigramme	= 0.100 "		
1 Decagramme	= 10 "	1 Centigramme	= 0.010 "		
1 Gramme	= 1 "	1 Milligramme	= 0.001 "		

			Logarithms.	Ar. Co. Log.
1 Kilogramme	= 2.20462 Pounds Avoirdupois.		0.3433 337	9.6566 663
1 "	= 2.67922 " Troy.		0.4280 083	9.5719 917
1 Gramme	= 15.43235 Grains.		1.1884 321	8.8115 679
1 Crith	= 0.089578 Grammes.		8.9522 014	1.0477 986

TABLE II.

ELEMENTARY ATOMS.

ALPHABETICAL LIST.

Aluminum,	Al	27.0 *	Molybdenum,	Mo	96.
Antimony,	Sb	120.0	Nickel,	Ni	58.8
Arsenic,	As	75.	Nitrogen,	N	14.0
Barium,	Ba	137.1	Norwegium (?)	Ng	145.9 ?
Bismuth,	Bi	210.0	Osmium,	Os	199.2
Boron,	B	11.0	Oxygen,	O	16.0
Bromine,	Br	80.0	Palladium,	Pa	106.6
Cadmium,	Cd	112.3	Phosphorus,	P	31.0
Cæsium,	Cs	133.	Platinum,	Pt	194.8
Calcium,	Ca	40.0	Potassium,	K	39.1
Carbon,	C	12.0	Rhodium,	Rh	104.4
Cerium,	Ce	141.0 *	Rubidium,	Rb	85.4
Chlorine,	Cl	35.5	Ruthenium,	Ru	104.4
Chromium,	Cr	52.2	Scandium,	Sc	44. *
Cobalt,	Co	58.8	Selenium,	Se	79.2
Columbium,	Cb	94.	Silicon,	Si	28.
Copper,	Cu	63.3	Silver,	Ag	108.0
Decipium (?)	Dp	159. *	Sodium,	Na	23.0
Didymium,	D	140. *	Strontium,	Sr	87.6
Erbium,	Er	167. *	Sulphur,	S	32.0
Fluorine,	F	19.0	Tantalum,	Ta	182.
Gallium,	Ga	70.0 *	Tellurium,	Te	128.
Glucinum,	Gl	13.9 *	Terbium (?)	Tr	171. ?*
Gold,	Au	197.	Thallium,	Tl	204.1
Holmium (?)	Ho	162. ?*	Thorium,	Th	231.4
Hydrogen,	H	1.00	Thulium (?)	Tm	170. ?*
Indium,	In	113.7 *	Tin,	Sn	118.
Iodine,	I	126.8	Titanium,	Ti	50.0
Iridium,	Ir	192.7	Tungsten,	Wo	184.
Iron,	Fe	56.0	Uranium,	Ur	120.
Lanthanum,	La	139. *	Vanadium,	V	51.3
Lead,	Pb	206.9	Ytterbium (?)	Yb	173. ?*
Lithium,	Li	7.0	Yttrium,	Y	91. ?*
Magnesium,	Mg	24.0	Zinc,	Zn	65.2
Manganese,	Mn	55.0	Zirconium,	Zr	89.6
Mercury,	Hg	200.0			

* On the assumption that the principal oxide is R_2O_3.

TABLE III.

SPECIFIC GRAVITY OF GASES AND VAPORS.

Names.	Symbols.	Sp. Gr. Air = 1.	Sp. Gr. $H_2 = 1$.	Half Molecular Weight.*	Logarithms†
Air	—	1.000	14.43	—	1.1593
Hydrogen	H_2	0.0693	1.00	1.00	0.0000
Acetylic Hydride (Aldehyde)	C_2H_4O	1.532	22.10	22.00	1.3424
Acetylic Chloride	C_2H_3OCl	2.87	41.42	39.25	1.5938
Acetic Anhydride	$C_4H_6O_3$	3.47	50.07	51.00	1.7076
Acetic Acid	$C_2H_4O_2$	2.083	30.07	30.00	1.4771
Aluminic Chloride	Al_2Cl_6	9.34	134.8	133.5	2.1255
Aluminic Bromide	Al_2Br_6	18.62	268.7	267.0	2.4265
Aluminic Iodide	Al_2I_6	27.	389.6	407.4	2.6100
Antimonious Chloride	$SbCl_3$	7.8	112.7	113.2	2.0540
Antimonious Oxide	Sb_4O_6	19.8	285.7	288.0	2.4594
Triethylstibine	$Sb(C_2H_5)_3$	7.23	104.4	103.5	2.0149
Arsenic	As_4	10.2	147.2	150.0	2.1761
Arseniuretted Hydrogen	AsH_3	2.695	38.90	39.00	1.5911
Arsenious Chloride	$AsCl_3$	6.3	90.90	90.75	1.9578
Arsenious Iodide	AsI_3	16.1	232.4	227.7	2.3574
Arsenious Oxide	As_4O_6	13.8	199.8	198.0	2.2967
Triethylarsine	$As(C_2H_5)_3$	5.29	76.35	81.00	1.9085
Kakodyl	$As_2(CH_3)_4$	7.10	102.5	105.0	2.0212
Bismuthous Chloride	$BiCl_3$	11.35	163.9	158.2	2.1994
Boric Methide	$B(CH_3)_3$	1.931	27.90	28.00	1.4472
Boric Ethide	$B(C_2H_5)_3$	3.401	49.10	49.00	1.6902
Boric Fluoride	BF_3	2.37	34.20	34.00	1.5315
Boric Chloride	BCl_3	3.942	56.85	58.75	1.7690
Boric Bromide	BBr_3	8.78	126.8	125.5	2.0986
Methylic Borate	$(CH_3)_3O_3B$	3.59	51.80	52.00	1.7160
Ethylic Borate	$(C_2H_5)_3O_3B$	5.14	74.20	73.00	1.8633
Bromine	Br_2	5.54	79.50	80.00	1.9031
Hydrobromic Acid	HBr	2.71	39.10	40.50	1.6075
Cadmium	Cd	3.94	56.85	56.15	1.7493
Cadmic Bromide	$CdBr_2$	9.25	133.5	136.1	2.1340
Carbonic Tetrachloride	CCl_4	5.415	78.14	77.00	1.8865
Phosgene Gas	$COCl_2$	3.399	49.06	49.50	1.6946
Dicarbonic Hexachloride	C_2Cl_6	8.157	117.7	118.5	2.0737
Dicarbonic Tetrachloride	C_2Cl_4	5.82	84.00	83.00	1.9191
Dicarbonic Dichloride	C_2Cl_2	—	—	47.50	1.6767
Carbonic Oxide	CO	0.967	13.95	14.00	1.1461

* Calculated from the atomic weights of Table II.

† By adding to these logarithms the constant 8.9622 we obtain the logarithms of the weight in grammes (under standard conditions) of one litre of each gas or vapor. (See page 70.)

Names.	Symbols.	Sp. Gr. Air = 1.	Sp. Gr $H_2 = 1$.	Half Molecular Weight.	Logarithms.
Carbonic Dioxide	CO_2	1.529	22.06	22.00	1.3424
Carbonic Disulphide	CS_2	2.645	38.17	38.00	1.5798
Chlorine	Cl_2	2.44	35.22	35.50	1.5502
Hydrochloric Acid	HCl	1.27	18.32	18.25	1.2613
Chromic Oxichloride	CrO_2Cl_2	5.5	79.4	77.60	1.8935
Columbic Chloride	$CbCl_5$	9.6	138.6	135.7	2.1326
Columbic Oxichloride	$CbOCl_3$	7.9	114.0	108.2	2.0342
Cuprous Chloride	Cu_2Cl_2	7.05	101.7	98.80	1.9948
Cyanogen Gas	$(CN)_2$	1.806	26.06	26.00	1.4150
Hydrocyanic Acid	HCN	0.947	13.67	13.50	1.1303
Cyanogen Chloride	CNCl	2.13	30.74	30.75	1.4878
Cyanic Acid	CNOH	1.50	21.65	22.50	1.3522
Ethyl	$(C_2H_5)_2$	2.00	28.86	29.00	1.4624
Ethylic Chloride	C_2H_5Cl	2.219	32.02	32.25	1.5085
Ethylic Oxide (Ether)	$C_4H_{10}O$	2.586	37.32	37.00	1.5682
Ethylic Hydrate (Alcohol)	C_2H_6O	1.613	23.28	23.00	1.3617
Ethylene (Olefiant Gas)	C_2H_4	0.978	14.11	14.00	1.1461
Ethylene Chloride	$C_2H_4Cl_2$	3.443	49.69	49.50	1.6946
Ethylene Oxide	C_2H_4O	1.422	20.52	22.00	1.3424
Ethylene Hydrate (Glycol)	$C_2H_6O_2$	—	—	31.00	1.4914
Ferric Chloride	Fe_2Cl_6	11.14	160.7	162.5	2.2108
Iodine below 700°	I_2	8.716	125.7	126.8	2.1031
Iodine above 1400°	I	4.6	66.4	63.4	1.8021
Hydriodic Acid	HI	4.443	64.12	63.9	1.8055
Indium Chloride	$InCl_2$	7.78	112.3	110.1	2.0418
Lead Chloride	$PbCl_2$	9.5	137.1	138.9	2.1427
Lead Methide	$Pb(CH_3)_4$	9.6	138.6	133.5	2.1255
Methyl Hydride (Marsh Gas)	CH_4	0.5576	8.05	8.00	0.9031
Methyl Chloride	CH_3Cl	1.736	25.05	25.25	1.4023
Methyl Bromide	CH_3Br	3.253	46.95	47.50	1.6767
Methyl Iodide	CH_3I	4.883	70.47	70.90	1.8506
Chloroform	$CHCl_3$	4.20	60.60	59.75	1.7763
Mercury	Hg	6.976	100.7	100.0	2.0000
Mercuric Ethide	$Hg(C_2H_5)_2$	9.97	143.9	129.0	2.1106
Mercuric Methide	$Hg(CH_3)_2$	8.29	119.6	115.0	2.0607
Mercuric Chloride	$HgCl_2$	9.8	141.5	135.5	2.1319
Mercuric Bromide	$HgBr_2$	12.16	175.6	180.0	2.2553
Mercuric Iodide	HgI_2	15.9	229.6	227.0	2.3560
Mercurous Chloride	Hg_2Cl_2	8.21	118.5	235.5	2.3720
Molybdic Chloride	$MoCl_5$	9.46	136.6	136.3	2.1345
Nitrogen	N_2	0.971	14.00	14.00	1.1461
Ammonia	NH_3	0.591	8.535	8.51	0.9294

Names.	Symbols.	Sp. Gr. Air = 1.	Sp. Gr. $H_2 = 1$.	Half Molecular Weight.	Logarithms.
Methylamine	$NH_2(CH_3)$	1.08	15.59	15.50	1.1903
Aniline	$NH_2(C_6H_5)$	3.21	46.33	46.50	1.6675
Nitrous Oxide	N_2O	1.527	22.04	22.00	1.3424
Nitric Oxide	NO	1.038	14.97	15.00	1.1761
Nitric Peroxide	NO_2	1.72	24.82	23.00	1.3617
Osmic Tetroxide	OsO_4	8.89	128.3	131.6	2.1193
Oxygen	O_2	1.1056	15.95	16.00	1.2041
Aqueous Vapor	H_2O	0.6235	8.998	9.00	0.9542
Phosphorus	P_4	4.42	63.78	62.00	1.7924
Phosphuretted Hydrogen	PH_3	1.184	17.09	17.00	1.2304
Phosphorus Chloride	$POCl_3$	4.742	68.44	68.75	1.8373
Phosphoric Oxichloride	PCl_3	5.3	76.49	76.75	1.8851
Phosphoric Sulphochloride	$PSCl_3$	5.88	84.86	84.75	1.9281
Oxide of Triethylphosphine	$PO(C_2H_5)_3$	4.6	66.39	67.00	1.8261
Selenium at 771°	Se_2	5.68	81.96	79.20	1.8987
Seleniuretted Hydrogen	H_2Se	2.795	40.33	40.60	1.6085
Silicic Methide	$Si(CH_3)_4$	3.083	44.49	44.00	1.6435
Silicic Ethide	$Si(C_2H_5)_4$	5.13	74.03	72.00	1.8573
Silicic Fluoride	SiF_4	3.600	51.95	52.00	1.7160
Silicic Chloride	$SiCl_4$	5.939	85.72	85.00	1.9294
Ethylic Silicate	$SiO_4(C_2H_5)_4$	7.32	105.6	104.0	2.0170
Stannic Ethide	$Sn(C_2H_5)_4$	8.021	115.8	117.0	2.0682
Stannic Dimethylo-diethide	$Sn(CH_3)_2(C_2H_5)_2$	6.838	98.68	103.0	2.0128
Stannic Chloro-triethide	$Sn(C_2H_5)_3Cl$	8.430	121.7	120.2	2.0799
Stannic Dichloro-diethide	$Sn(C_2H_5)_2Cl_2$	8.710	125.7	123.5	2.0917
Stannic Chloride	$SnCl_4$	9.199	132.7	130.0	2.1139
Stannous Chloride	Sn_2Cl_4	13.08	188.7	189.0	2.2765
Sulphur above 860°	S_2	2.23	32.18	32.00	1.5051
Sulphur at 450°	S_6	6.617	95.50	96.00	1.9823
Sulphuretted Hydrogen	H_2S	1.191	17.19	17.00	1.2304
Sulphurous Oxide	SO_2	2.234	32.24	32.00	1.5051
Sulphuric Oxide	SO_3	2.763	39.87	40.00	1.6021
Sulphurylic Chloride	SO_2Cl_2	4.67	67.39	67.50	1.8293
Tantalic Chloride	$TaCl_5$	12.8	184.7	179.7	2.2546
Thallium Chloride	$TlCl$	8.2	118.3	119.8	2.0785
Titanic Chloride	$TiCl_4$	6.836	98.65	96.00	1.9823
Tungsten Pentachloride	$WoCl_5$	12.7	183 2.	180.7	2.2570
Tungsten Hexachloride	$WoCl_6$	13.2	190.5	198.5	2.2978
Tungsten Oxichloride	$WoOCl_4$	11.84	170.9	171.0	2.2330
Vanadium Tetrachloride	$VaCl_4$	6.69	96.54	96.65	1.9852
Vanadium Oxichloride	$VaOCl_3$	6.11	88.16	86.90	1.9390
Zinc Methide	$Zn(CH_3)_2$	3.29	47.47	47.60	1.6776
Zinc Ethide	$Zn(C_2H_5)_2$	4.26	61.46	61.60	1.7896
Zinc Chloride	$ZnCl_2$	4.57	65.95	68.10	1.8331

TABLE IV.

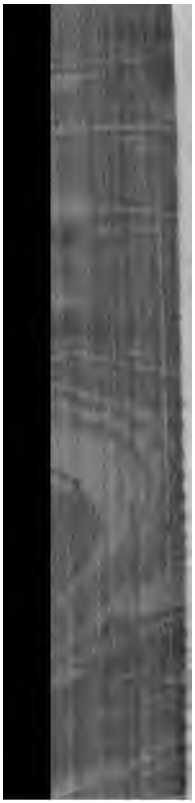
SPECIFIC HEAT OF ELEMENTARY SUBSTANCES.

Name.	Specific Heat.	Temperature.	Atomic Weight.	Product.
Aluminium	0.2314	60°	27	3.1
Antimony	0.0508	55°	120	6.1
Arsenic (crystallized)	0.0814	61°	75	6.1
Bismuth	0.0308	55°	210	6.5
Boron (in square octahedral crystals)	0.2500	230°	11	2.8
Cadmium	0.0548	87°	112	6.1
Calcium	0.1700	59°	40	6.8
Carbon (Diamond)	0.1650	995°	12	1.9
Cerium	0.0448	46°	141	6.3
Cobalt	0.1067	55°	59	6.3
Copper	0.0952	36°	63	6.0
Didymium	0.0728	26°	140	6.1
Erbium	0.402	24°	112.9	5.0
Gold	0.0324	55°	197	6.4
Iridium	0.0579	50°	193.7	6.3
Iridium	0.0543	55°	197	6.9
Iridium	0.0326	61°	193.7	6.4
Iron	0.1124	58°	56	6.4
Lanthanum	0.0449	54°	139	6.2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE V.

HEAT OF COMBINATION.

Name.	Constituents.	Condition of Product.			
		Gas.	*Liquid.*	*Solid.*	*Solution.*
Hydrochloric Acid.....	$H + Cl$	+22.0	.....	.....	+39.3
Potassic Chloride	$K + Cl$	.....	.....	+105.6	+101.2
Magnesic Chloride	$Mg + Cl_2$	.....	.....	+151.0	+187.0
Aluminic Chloride.....	$Al + Cl_3$	.....	.....	+160.9	+237.8
Hydrobromic Acid.....	$H + Br$	+8.4	.....	.....	+28.4
Hydriodic Acid	$H + I$	−6.2	.....	.....	+13.2
Chloric Acid	$Cl + O_3 + H$	.....	.....	.....	+22.5
Potassic Chlorate	$Cl + O_3 + K$	.....	.....	+94.6	.....
Water	$H_2 + O$	+59.4	+69.0	+70.4	.....
Potassic Hydrate	$K + O + H$	.....	.....	+104.3	+116.8
Sodic Hydrate.....	$Na + O + H$	.....	.....	+102.8	+112.1
Magnesic Hydrate	$Mg + O_2 + H_2$	.....	.....	+218.0	.....
Hydric Peroxide.....	$H_2 + O_2$	.....	.....	.....	+46.6
Hydric Sulphide.....	$H_2 + S$	+4.6	.....	.....	+9.2
Nitrogen Chloride	$N + Cl_3$	.....	−38.1	.....	.....
Ammonia.....	$H_3 + N$	+26.7	.....	.....	+35.2
Ammonic Chloride.....	$N + H_4 + Cl$	.....	.....	+91.2	+87.3
Ammonic Nitrate	$N_2 + H_4 + O_3$	.....	.....	+80.7	.....
Nitrous Oxide.....	$N_2 + O$	−18.0	−13.6	.....	.....
Nitric Oxide	$N + O$	−43.3	.....	.....	.....
Nitrous Anhydride ...	$N_2 + O_3$	−65.6	.....	.....	.....
Nitric Peroxide	$N + O_2$	−24.3	−20.0	.....	.....
Nitric Pentoxide	$N_2 + O_5$	−44.6	−39.8	−31.6	−14.8
Nitric Acid.....	$N + O_3 + H$	.....	+19.6	.....	+27.1
Potassic Nitrate	$K + N + O_3$	.....	.....	+97.0	.....
Sodic Nitrate	$Na + N + O_3$	.....	.....	+88.6	.....
Argentic Nitrate.....	$Ag + N + O_3$	.....	.....	+6.5	.....
Sulphurous Oxide	$S + O_2$	+69.1	.....	.....	+76.8
Sulphuric Oxide.....	$S + O_3$	.....	.....	+103.6	+141.0
Sulphuric Acid	$S + O_4 + H_2$	.....	+193.0	+194.0	+210.0
Potassic Sulphate	$K_2 + S + O_4$	.....	.....	+342.2	+336.2
Sodic Sulphate	$Na_2 + S + O_4$	.....	.....	+326.4	+327.2
Zincic Sulphate	$Zn + S + O_4$	.....	.....	+233.4	+252.0
Cupric Sulphate	$Cu + S + O_4$	.....	.....	+182.8	+199.1
Phosphoric Oxide	$P_2 + O_5$	.....	.....	+363.8	+405.4



[illegible]	$C + O_2$	+ 94.0	.....
[illegible]	$C + O_2$	+ 97.0	.....
[illegible]			
[illegible]	C + O	+ 25.0	.....
[illegible]	C + O	+ 28.0	.....
[illegible]			
[illegible]	Si + O_2	.....	.....
[illegible]	Si + O_2	.....	.....
[illegible] Oxide	Sn + O	.....	.....
[illegible] Oxide	Sn + O_2	.....	.....
[illegible] Oxide	Fe + O	.....	.....
[illegible] Oxide	$Fe_2 + O_3$	.....	.....
[illegible] Oxide	Mn + O	.....	.....
[illegible] Dioxide	Mn + O_2	.....	.....
[illegible] Oxide	Zn + O	.....	.....
[illegible] Oxide	Cu + O	.....	.....
[illegible] Oxide	Hg + O	.....	.....
[illegible] Oxide	Ag_2 + O	.....	.....
[illegible] Chloride	P + Cl_3	+ 68.9	+ 75.
[illegible] Chloride	P + Cl_5	.....	.....
[illegible] Oxichloride	P + Cl_3 + O	.....	+ 142.
[illegible]			
[illegible] Diamond	C + N	+ 41.0	.....
[illegible] Acid	C + N + H	+ 14.1	— 8.
[illegible] Cyanide	C + N + K	.....	.....

LOGARITHMS AND ANTILOGARITHMS.

15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
5	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
6	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
7	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
8	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
9	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
0	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
1	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
2	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
3	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
4	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
5	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
6	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
7	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
8	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
9	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Name.	Constituents.	Conditions of Product.			
		Gas.	*Liquid.*	*Solid.*	*Solution.*
Acetylene (C = Diam.)	$C_2 + H_2$	−64.0	.....	.....	.....
Ethylene "	$C_2 + H_4$	−8.0	.....	.....	.....
Marsh Gas	$C + H_4$	+22.0	.....	.....	.....
Carbonic Dioxide					
C = Diamond.....	$C + O_2$	+94.0	.....	+100.0	+99.6
C = Amorphous.....	$C + O_2$	+97.0	.....	+103.0	+102.6
Carbonic Oxide					
C = Diamond.....	C +O	+25.0	.....	.....	.....
C = Amorphous.....	C + O	+28.0	.....	.....	.....
Silicic Oxide					
Si = Crystallized....	$Si + O_2$	.....	.....	+227.3	.....
Si = Amorphous.....	$Si + O_2$	.....	.....	+219.2	.....
Stannous Oxide	Sn + O	.....	.....	+70.2	.....
Stannic Oxide.....	$Sn + O_2$	.....	.....	+141.2	.....
Ferrous Oxide..... ..	Fe + O	.....	.....	+68.2	.....
Ferric Oxide	$Fe_2 + O_3$	.....	.....	+191.2	.....
Manganous Oxide	Mn + O	.....	.....	+94.8	.....
Manganic Dioxide	$Mn + O_2$	.....	.....	+116.2	.....
Zincic Oxide	Zn + O	.....	.....	+85.4	.....
Cupric Oxide	Cu + O	.....	.....	+37.2	.....
Mercuric Oxide	Hg + O	.....	.....	+30.6	.....
Argentic Oxide	$Ag_2 + O$	.....	.....	+6.0	.....
Phosphorous Chloride .	$P + Cl_3$	+68.9	+75.8	.....	.....
Phosphoric Chloride ...	$P + Cl_5$	.....	.....	+107.8	.....
Phosphoric Oxichloride	$P + Cl_3 + O$	.....	+142.4	.....	.....
Cyanogen					
C = Diamond.....	C + N	+41.0	.....	.....	.....
Prussic Acid	C + N + H	+14.1	−8.4	.....	+8.0
Potassic Cyanide	C + N + K	.....	.....	+45.7	+42.9
Mercuric Cyanide	$C_2 + N_2 + Hg$	.....	.....	−20.4	−23.4
Argentic Cyanide	C + N + Ag	.....	.....	−18.6	.....
Ozone	$O_2 + O$	−29.6	.....	.....	.....

LOGARITHMS AND ANTILOGARITHMS.

LOGARITHMS OF NUMBERS.

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	5	6	7

0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
										1	2	3	4	5	6	7	8	9
7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS.

Logarithms.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	3	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	2	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	2	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	2	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	2	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	6
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	6	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	5	5	6	7

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
0	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
1	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
2	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
3	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
4	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
5	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
6	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
7	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
8	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
9	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
0	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
1	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
2	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
3	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
4	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
5	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
6	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
7	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
8	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
9	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
0	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
1	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
2	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
3	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
4	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
5	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
6	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
7	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
8	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
9	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
0	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
1	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
2	6607	662-	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
3	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
4	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
5	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
6	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
7	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
8	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
9	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
0	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
1	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
2	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
3	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
4	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
5	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
6	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
7	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
8	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
9	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

CONSTANT LOGARITHMS.

		Logarithms.	Ar. Co. Log.
Circumf. of circle when $R = 1$,	$(2\pi = 6.2832)$	0.7982	9.2018
" " " " $D = 1$,	$(\pi = 3.1416)$	0.4971	9.5028
Area of circle when $R^2 = 1$,	$(\pi = 3.1416)$	0.4971	9.5028
" " " " $D^2 = 1$,	$(\frac{\pi}{4} = 0.7854)$	9.8951	0.1049
" " " " $C^2 = 1$,	$(\frac{1}{4\pi} = 0.0796)$	8.9008	1.0992
Surface of sphere when $R^2 = 1$,	$(4\pi = 12.5664)$	1.0992	8.9008
" " " " $D^2 = 1$,	$(\pi = 3.1416)$	0.4971	9.5028
" " " " $C^2 = 1$,	$(\frac{1}{\pi} = 0.3183)$	9.5028	0.4971
Solidity of sphere when $R^3 = 1$,	$(\frac{4}{3}\pi = 4.1888)$	0.6221	9.3779
" " " " $D^3 = 1$,	$(\frac{\pi}{6} = 0.5236)$	9.7190	0.2810
" " " " $C^3 = 1$,	$(\frac{1}{6\pi^2} = 0.0169)$	8.2275	1.7724
Weight of one litre of Hydrogen	(0.0896 grammes)	8.9522	1.0478
" " " " " Air	(1.293 ")	0.1116	9.8884
" " " " " "	(14.43 criths)	1.1594	8.8406
Per cent of Oxygen in air by weight	(0.2318)	9.3651	0.6349
" " " Nitrogen " " " "	(0.7682)	9.8855	0 1145
Mean height of Barometer	(76 c. m.)	1.8808	8.1192
Coefficient of expansion of Air	(0.00366)	7.5635	2.4365
Latent Heat of Water	(79)	1.8976	8.1024
" " " Free Steam	(537)	2.7300	7.2700
To reduce Sp.Gr. to Sp. Gr., or reverse, add to log.		1.1594 or	8.8406
" " Sp. Gr. to *Sp. Gr.*, " " " " "		5.9522 or	4.0478
" " Sp.Gr. to *Sp. Gr.*, " " " " "		7.1116 or	2.8884
" " grammes to criths, " " " " "		1.0478 or	8.9522

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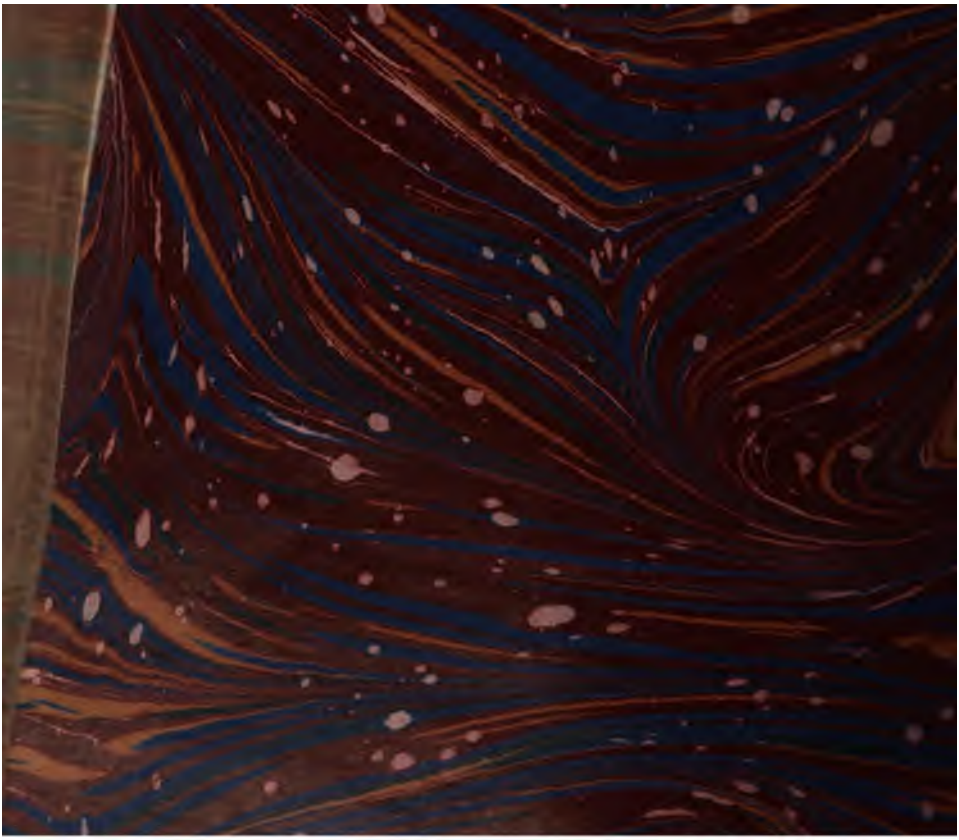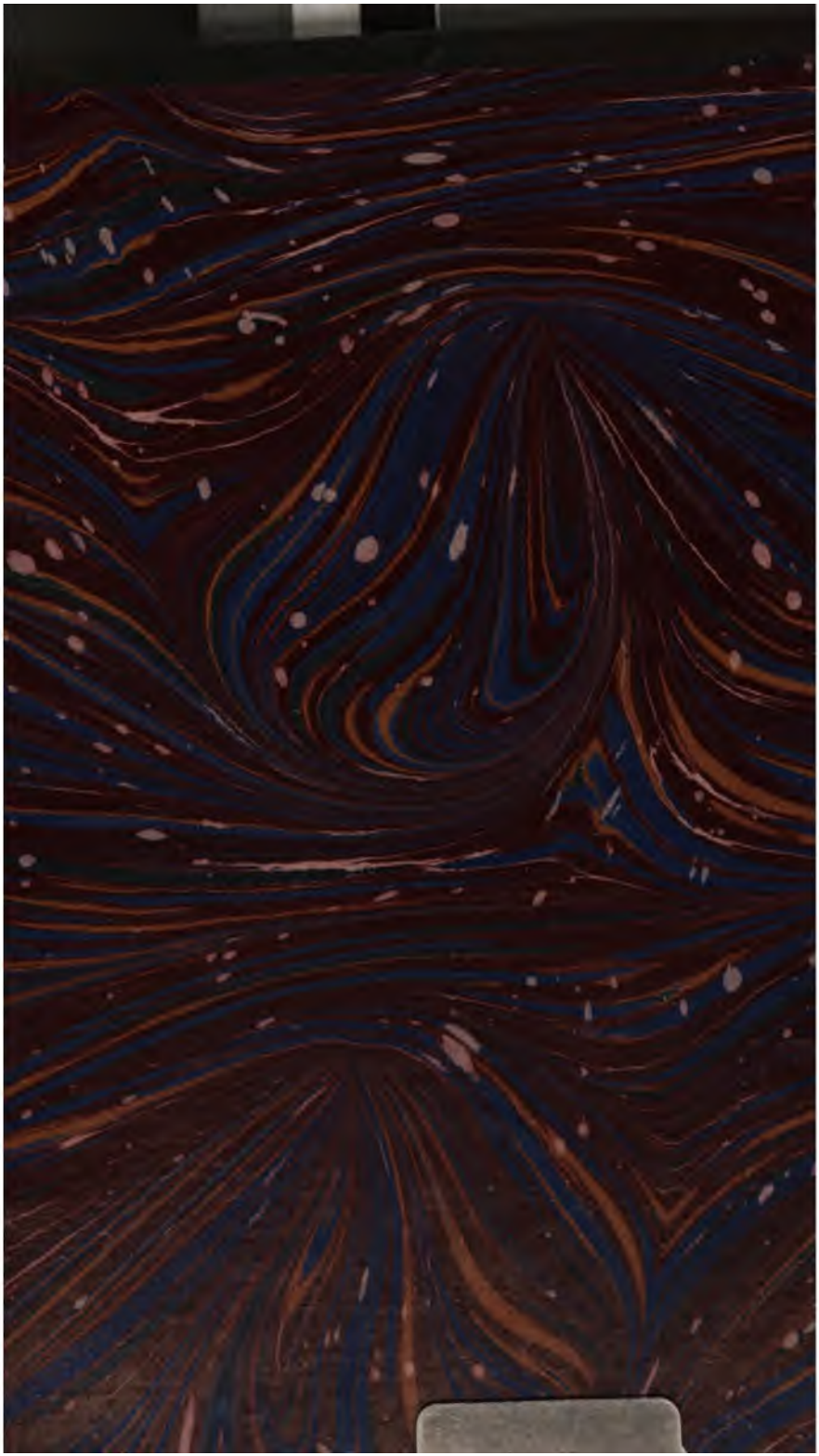
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